Biomass and Bioenergy 217 (2027) 110334

Contents lists available at ScienceDirect

Biomass and Bioenergy

journal homepage: www.elsevier.com/locate/biombioe

Biochar-based catalysts and catalyst supports for biodiesel production: Structure-performance relationships and perspectives for South Africa

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ARTICLE INFO

Keywords:
Biochar
Biodiesel
Heterogeneous catalysis
Surface functionalisation
Catalyst supports
Structure-performance relationships
Biomass valorisation
Circular bioeconomy

ABSTRACT

The development of efficient, recoverable, and reusable heterogeneous catalysts is critical for sustainable biodiesel production, particularly from low-cost lipid feedstocks containing high concentrations of free fatty acids. Biochar has attracted increasing attention as both a catalyst and catalyst support because its pore architecture, surface chemistry, mineral composition, and acid–base properties can be tailored through feedstock selection, pyrolysis, activation, functionalisation, and active-phase incorporation. This review critically evaluates biochar-based catalysts and catalyst supports for biodiesel production, with emphasis on the relationships between physicochemical properties and catalytic performance in esterification, transesterification, and bifunctional reaction systems. Evidence from the literature indicates that catalytic activity is governed by the combined effects of pore connectivity, active-site density and accessibility, surface functionality, active-phase dispersion, and structural stability rather than by surface area alone. However, differences in feedstock composition, catalyst-preparation methods, reaction conditions, and performance-reporting protocols currently limit direct quantitative comparisons and the establishment of universal design thresholds. The review further examines catalyst deactivation, regeneration, and reusability, and compares biochar with activated carbon, mesoporous silica, zeolites, and metal oxides in terms of catalytic properties, preparation requirements, stability, and downstream process compatibility. South Africa is presented as a case study for aligning locally available biomass residues and potential lipid feedstocks with biochar-based catalyst development. Remaining challenges include feedstock variability, active-site leaching, catalyst lifetime, process scale-up, techno-economic feasibility, and life-cycle sustainability. Accordingly, a staged research framework is proposed to guide laboratory validation, pilot-scale assessment, and the eventual industrial implementation of biochar-based biodiesel catalysts in South Africa and other biomass-rich regions.

1. Introduction

The transition toward carbon-neutral energy systems has intensified research into renewable liquid fuels that can replace petroleum-derived diesel. Biodiesel has emerged as one of the most promising alternatives because it is biodegradable, renewable, and compatible with existing diesel engines [1–4].

Advanced catalysis is widely recognised as a key enabling technology in the transition towards a sustainable, low-carbon economy, mediating 85–90% of modern industrial chemical transformations. Within the biofuel sector, the historical reliance on traditional homogeneous catalysts - such as liquid mineral acids (H_2SO_4) or strong bases (NaOH, KOH) - has led to significant process inefficiencies. These liquid-phase systems cannot be readily recovered, require water-intensive neutralisation and washing steps, and pose severe saponification risks when exposed to low-grade, high-free-fatty-acid (FFA) waste lipids. To overcome these operational barriers, the green energy industry has shifted its focus toward heterogeneous support architectures. While conventional synthetic matrices such as mesoporous silica (SBA-15), engineered zeolites, and alumina offer well-defined porosity and high surface areas, their wider sustainability and cost performance can be constrained by energy-intensive preparation or template-removal processes, precursor requirements, and manufacturing costs [5–9].

Concurrently, biochar has emerged as a structurally versatile, cost-

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https://doi.org/10.1016/j.biombioe.2026.110334
Received 2 September 2026; Received in revised form 4 November 2026; Accepted 20 November 2026
Available online 25 November 2026
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effective, and potentially lower-carbon, biomass-derived alternative to these conventional engineered supports and may contribute to carbon retention when production and end-of-life conditions are appropriately managed. Produced via the controlled thermochemical pyrolysis of lignocellulosic biomass residues under oxygen-limited or inert conditions, biochar inherently possesses a robust polycyclic aromatic carbon framework. The role of biochar within a carbon-neutral bioeconomy extends beyond carbon storage to include renewable energy generation, biomass valorisation, and mitigation of net atmospheric CO_2 emissions, as illustrated in Fig. 1. Moreover, this carbon matrix can be tailored to exhibit hierarchical porosity, abundant surface-oxygenated functional groups, and stable inorganic mineral phases that enhance catalytic activity [10–12].

The growing scientific interest in biochar has led to numerous reviews examining its physicochemical properties and applications across a wide range of environmental and catalytic processes. For example, the landmark works of Tan et al. (2016) [14] and Xiong et al. (2017) [15] comprehensively detailed the broad material chemistry of biochar across environmental remediation, carbon storage, and generic chemical synthesis pathways. More recently, focused reviews by El-Fawal et al. (2025) [16] and Zohmingliana et al. (2024) [17] evaluated the general transition of lignocellulosic waste into carbonaceous matrices for biofuel applications.

Recent experimental studies demonstrate that biomass-derived carbon catalysts are progressing beyond conventionally sulfonated biochars towards materials with controlled acidity, hierarchical structures, atomically dispersed active sites, and photothermal functionality. Huang et al. [18] prepared a lignin-derived layered three-dimensional biochar with tunable acidity that produced a maximum biodiesel yield of 97.2% from *Jatropha oil*, with the reported yield remaining above 90% after four reuse cycles. A biomass-derived SO_3H-functionalised graphene-like catalyst subsequently enabled photothermal conversion of microalgal lipids at room temperature, achieving a biodiesel yield of 96.8% [19]. Further development of graphene-like biomass-derived catalysts containing neighbouring potassium or caesium single atoms enabled reported biodiesel yields of 99.6% and above 97%, respectively, under ambient photothermal conditions [20,21]. These studies illustrate the progression from bulk surface functionalisation towards control of active-site configuration and local reaction environments. Nevertheless, direct comparison remains difficult because the studies used different lipid feedstocks, catalyst formulations, irradiation conditions, reaction times, performance metrics, and stability-assessment procedures.

Parallel advances in non-biochar heterogeneous catalysts further demonstrate the importance of controlling pore accessibility, surface acidity, interfacial interactions, and the local catalytic environment. He et al. [22] developed an organic-modified mesoporous montmorillonite catalyst that produced a maximum biodiesel yield of 97.02%. In a subsequent study, He et al. [23] reported that a g-C_3N_4–TiO_2/montmorillonite photocatalyst achieved a biodiesel yield of 98.5% through modulation of the photocatalytic microenvironment. More recently, Wang et al. [24] used cluster-defect engineering to increase the hierarchical porosity and Lewis-acid-site availability of UiO-66, resulting in a reported biodiesel yield of 99.3% during visible-light-assisted oleic acid esterification. Zhou et al. [25] similarly developed a cellulose-derived sulfonated hydrochar that achieved a reported biodiesel yield of 98.29% from non-edible oil within 30 min under simulated solar irradiation. Although these materials do not all fall within the strict definition of pyrolysis-derived biochar, they provide relevant evidence that catalytic performance depends on the interaction among active-site chemistry, reactant accessibility, mass transfer, and the reaction microenvironment rather than on surface area alone. They therefore provide important benchmarks against which the design and performance of biochar-based catalysts should be assessed.

However, despite this growing body of literature, the combined relationships among biomass origin, preparation conditions, pore architecture, surface chemistry, active-site accessibility, catalyst stability, and process compatibility have received comparatively limited critical treatment. Recent reviews have provided valuable summaries of biochar preparation, functionalisation, catalytic applications, and biodiesel yields [16,17]. The present review builds on these contributions by examining why apparently similar biochar-based materials exhibit different catalytic behaviour and by evaluating whether commonly reported descriptors, including BET surface area, morphology, and total acid or base density, are sufficient predictors of catalytic performance. Particular attention is given to the influence of feedstock-derived structure and mineral composition, pyrolysis and activation conditions, the accessibility and stability of active sites, and the interactions among these properties during esterification and transesterification.

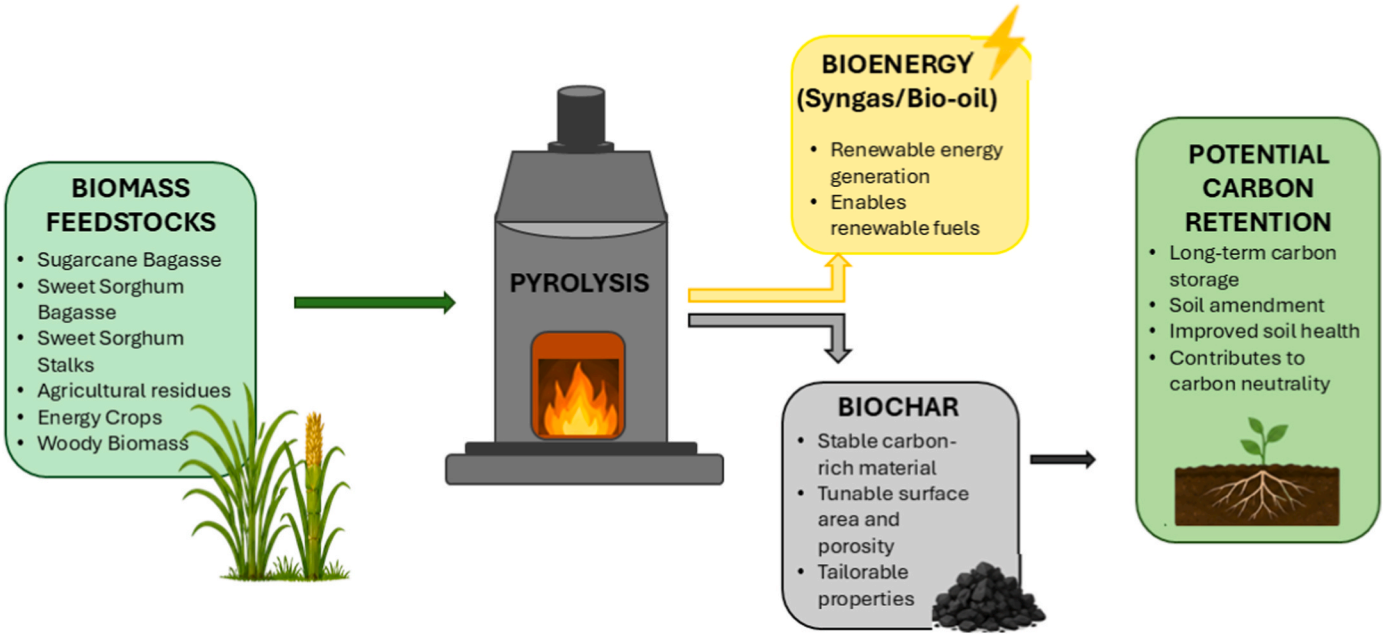


Fig. 1. Schematic representation of the potential role of biochar in a carbon-neutral bioeconomy, illustrating the conversion of biomass feedstocks through pyrolysis into biochar and bioenergy (syngas and bio-oil), highlighting renewable energy generation and long-term carbon sequestration. Adapted from Ref. [13].

In this review, "biochar-based catalyst" is used as an umbrella term encompassing two related but distinct catalytic roles. A biochar-supported catalyst is defined as a system in which the carbon matrix primarily acts as a carrier or stabilising scaffold for an introduced active phase, such as a metal, metal oxide, enzyme, or other catalytically active species. In contrast, a functionalised or directly catalytic biochar derives activity from native mineral constituents or from catalytic groups incorporated onto the carbon framework, such as $–SO_3H$, carboxylic, or basic surface functionalities. Some materials combine these roles by providing both intrinsic surface activity and support for an additional active phase. This distinction is maintained throughout the review because it determines whether observed catalytic performance and deactivation are attributed to the carbon support, the introduced active phase, or the intrinsic catalytic components of the biochar.

The novelty of this review lies in integrating four elements that are commonly considered separately. First, it critically links feedstock origin, thermochemical processing, pore connectivity, surface functionality, and active-site accessibility to catalytic performance rather than cataloguing biodiesel yields alone. Secondly, it compares biochar with activated carbon, mesoporous silica, zeolites, and metal oxides using material and process-level considerations, including catalyst separation, regeneration, and compatibility with downstream biodiesel purification. Thirdly, it distinguishes simple catalyst reuse from evidence of active-site stability by examining leaching, filtrate activity, spent-catalyst characterisation, and regeneration where such data are available. Finally, South Africa is used as a focused case study to connect locally available biomass resources with catalyst-development priorities, scale-up constraints, techno-economic and life-cycle requirements, and measurable research targets. These elements culminate in an integrated framework for advancing biochar-based biodiesel catalysts from material design towards pilot-scale validation in South Africa and other biomass-rich regions.

2. The evolving chemistry of biochar

Biochar has experienced a significant shift in scientific interest and utility. With advances in thermal conversion methods and post-treatment strategies, biochar has emerged as a chemically versatile material with increasing relevance in catalytic usage. Its intrinsic properties - such as porosity, surface area, and oxygenated surface functional groups - enable various physicochemical interactions important for catalysis [26]. Moreover, BC can be deliberately modified through chemical activation, surface oxidation, metal or metal-oxide loading, and acid or base treatments, thereby enhancing its reactivity and selectivity for targeted applications. As such, biochar is no longer viewed merely as a by-product of pyrolysis but as a tunable material platform capable of supporting or directly participating in reactions central to biodiesel conversion. This section discusses the structural evolution, surface chemistry, and functionalisation strategies that support biochar's catalytic potential.

2.1. Chemical mechanism of biochar formation

Biochar formation during pyrolysis involves sequential dehydration, devolatilisation, depolymerisation, and carbonisation reactions, as summarised in Fig. 2 [27]. Removal of moisture and thermally labile components at lower temperatures is followed by decomposition of hemicellulose and cellulose, release of volatile products, and progressive condensation of the remaining carbon framework. At higher temperatures, increasing aromatic condensation and partial graphitic ordering generally improve the thermal and chemical stability of the resulting biochar [28].

For catalytic applications, these transformations are important because they simultaneously determine pore development, surface functionality, mineral concentration, and the stability of the carbon framework. Increasing pyrolysis severity can promote pore formation and aromatic condensation, but can also remove oxygen-containing groups that provide anchoring sites for supported species or contribute to surface acidity. The appropriate pyrolysis conditions must therefore be selected according to whether the biochar is intended to act primarily as a porous support, an intrinsically active catalyst, or a precursor for subsequent acid, base, or metal functionalisation.

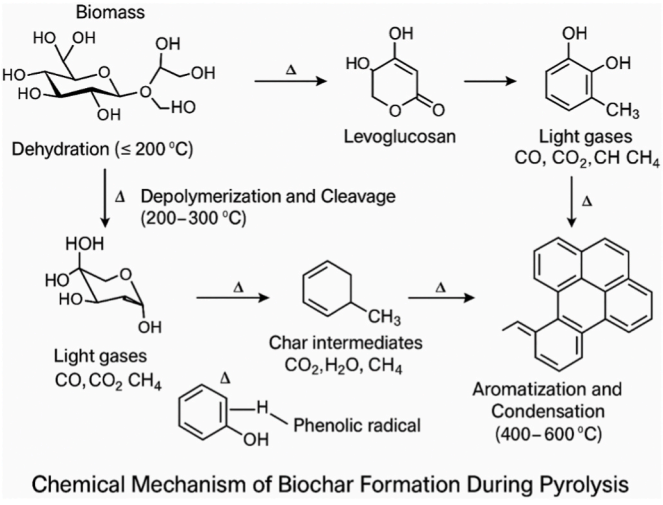


Fig. 2. Principal thermochemical transformations occurring during the conversion of lignocellulosic biomass into biochar by pyrolysis.

2.2. Structural and textural properties of biochar

The effectiveness of biochar as a catalyst or catalyst support depends on the accessibility and stability of its active regions rather than on surface area alone. Pore size distribution and connectivity control the transport of triglycerides, free fatty acids, alcohols, and products, while surface functional groups and retained mineral species determine the chemical character of the accessible sites. Morphology and carbon-framework stability additionally influence active-phase dispersion, resistance to pore collapse, and catalyst reuse.

These properties are governed principally by feedstock composition and thermochemical processing conditions. Feedstock determines the initial lignocellulosic structure and inorganic composition, whereas pyrolysis temperature, heating rate, residence time, atmosphere, and activation conditions regulate volatile removal, pore development, aromatic condensation, and surface functionality [29]. Table 1 summarises these variables in terms of their relevance to catalytic performance.

2.2.1. Biochar surface area and porosity

Surface area and pore architecture influence catalytic performance by controlling active-phase dispersion, active-site accessibility, and the transport of reactants and products. According to the IUPAC classification, biochar pores are categorised as micropores (<2 nm), mesopores (2–50 nm), and macropores (>50 nm), as illustrated in Fig. 3. Although micropores contribute substantially to the measured surface area, they may be inaccessible to bulky triglyceride molecules. Mesopores and macropores are therefore particularly important in biodiesel production because they facilitate the diffusion of triglycerides and free fatty acids towards catalytically active regions. An effective catalyst support consequently requires an interconnected and accessible pore network rather than merely a high total surface area [37–40].

Pore architecture can be adjusted through pyrolysis and subsequent activation or post-treatment. Albanese et al. (2019), for example, reported that hydrodynamic cavitation increased the surface area of slow-pyrolysis biochar produced at 550 °C by up to 120% without substantially altering its chemical integrity [41]. Nevertheless, an increase in surface area does not necessarily produce a proportional improvement

Table 1
Principal feedstock and pyrolysis parameters influencing the properties of biochar relevant to catalytic applications.

Parameter	Effect on biochar properties	Relevance to catalytic performance	Supporting studies
Feedstock composition	Determines the lignocellulosic structure, ash and mineral composition, carbon yield, and development of the pore network.	Influences intrinsic acid–base activity, pore accessibility, and the interaction between the carbon support and deposited active species. Biochars produced under identical pyrolysis conditions may therefore exhibit substantially different catalytic properties.	Edeh et al. [30]; Muigai et al. [31]
Pyrolysis temperature	Increasing temperature generally promotes devolatilisation, aromatic condensation, pore development, and carbon stability, while decreasing oxygen-containing surface groups.	Higher temperatures may produce more stable catalyst supports but can reduce functional groups required for reactant adsorption or active-phase anchoring. The optimum temperature, therefore depends on the intended functionalisation and catalytic reaction.	Tu et al. [32];
Heating rate and residence time	Slow heating and longer residence times generally favour char formation and carbon condensation, whereas rapid heating increases volatile production and may limit structural development.	These parameters affect catalyst yield, carbon-framework stability, pore development, and the retention of surface functionalities and minerals.	Mukherjee et al. [33]; Anupam et al. [34]
Reaction atmosphere and carrier-gas flow	Gas composition and flow influence volatile removal, secondary reactions, carbon gasification, and pore development.	Inadequate volatile removal can obstruct pore development, whereas excessively reactive conditions may reduce carbon yield or alter the surface chemistry and pore network.	Buss et al. [35]
Feedstock particle size	Controls heat and mass transfer during pyrolysis. Smaller particles generally heat more uniformly, whereas larger particles may retain more of the precursor's macroporous structure.	Non-uniform heating can produce chemically and structurally heterogeneous supports, affecting active-phase dispersion and reproducibility of catalytic performance.	Leng et al. [36]

in biodiesel yield because catalytic performance also depends on pore accessibility, surface chemistry, active-site density, and the distribution and stability of the supported phase. Porosity should therefore be evaluated together with these chemical and structural properties when designing biochar-based catalysts and catalyst supports.

2.2.2. Biochar morphology

Biochar morphology is strongly influenced by the anatomical structure and composition of the parent biomass. Lignocellulosic feedstocks may partially retain their original vascular channels, fibre bundles, and cellular arrangements following pyrolysis. Consequently, wood-derived

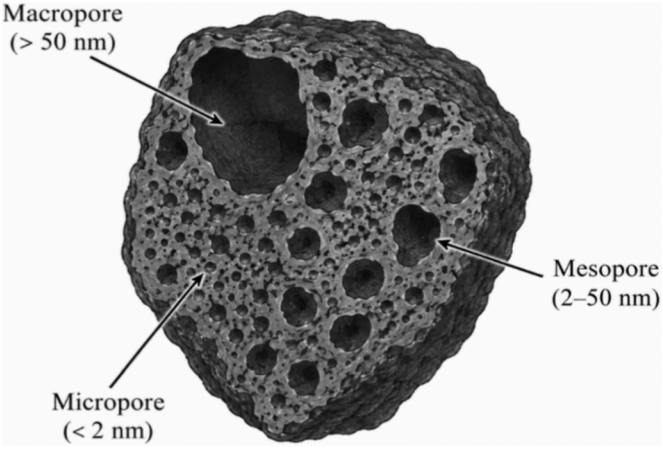


Fig. 3. Hierarchical pore structure of biochar, comprising micropores, mesopores, and macropores.

biochars frequently exhibit elongated channels and relatively ordered pore networks, whereas biochars derived from herbaceous residues may possess more fragmented and irregular structures [42–44]. Pyrolysis severity further determines whether these inherited features are retained, enlarged through volatile removal, or partially collapsed during carbonisation [45,46].

For catalytic applications, morphology is important because pore connectivity and surface accessibility influence reactant transport and the dispersion of supported active species. Interconnected channels can facilitate the movement of triglycerides, free fatty acids, alcohols, and products, while an accessible external surface can promote more uniform deposition of metals, metal oxides, or functional groups. Conversely, pore collapse, poorly connected internal regions, or blockage caused by excessive active-phase loading can limit access to otherwise active sites. Morphological characterisation should therefore be interpreted together with pore-size distribution, active-phase dispersion, and catalytic measurements rather than being used independently to predict catalyst performance [47–49].

2.2.3. Biomass feedstock for biochar

Feedstock selection influences the carbon structure, pore architecture, surface functionality, and inorganic composition of biochar. Lignocellulosic biomass consists principally of cellulose, hemicellulose, and lignin, as illustrated in Fig. 4, which undergo thermal decomposition over different temperature ranges. Their relative proportions affect volatile release, char yield, pore development, and aromatic condensation during pyrolysis [50–53]. Feedstock-derived inorganic constituents, including calcium, potassium, sodium, magnesium, phosphorus, and silicon, may also be retained or concentrated in the biochar. Depending on their chemical form and accessibility, these species can contribute catalytic sites, assist in anchoring a deposited active phase, or obstruct pores and dilute the catalytically useful carbon fraction [54–56].

The effect of feedstock composition was demonstrated by Muigai et al. (2020), who compared biochars derived from sugarcane bagasse, water hyacinth, and yellow oleander at 550 °C. Despite being produced under the same nominal temperature, the materials exhibited ash contents of 0.9–21.8% and carbon contents of 39.1–80.7%. Sugarcane bagasse produced a biochar with a surface area of 17.8 $m^2\ g^{-1}$, an average pore size of 12.9 nm, an ash content of 1.16%, and a carbon content of 77.4% [30]. These variations demonstrate that identical pyrolysis temperatures do not produce equivalent supports when the precursor composition differs. Feedstock selection should therefore consider not only carbon yield but also the pore structure, mineral content, surface chemistry, and compatibility of the resulting biochar with the intended active phase and biodiesel feedstock.

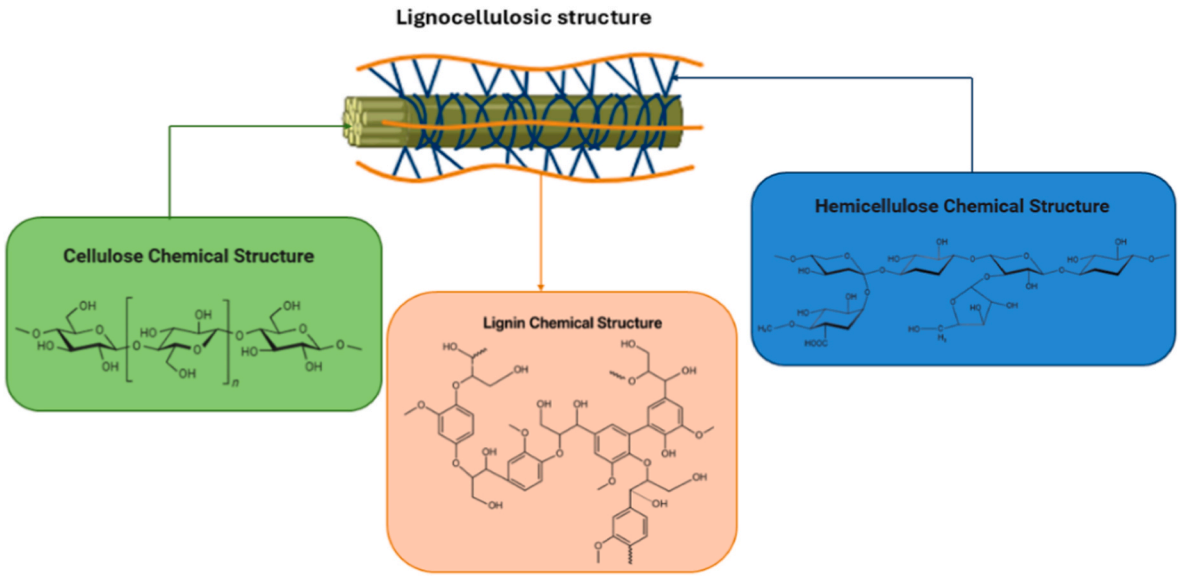


Fig. 4. Schematic representation of the lignocellulosic structure of biomass, illustrating its three principal structural components – cellulose, hemicellulose, and lignin – and their corresponding chemical structures. Adapted from Ref. [53].

2.2.4. *Effect of pyrolysis on biochar structure*

Pyrolysis temperature, heating rate, residence time, and atmosphere regulate the balance between pore development, surface functionality, mineral retention, and carbon-framework stability. Increasing pyrolysis temperature generally promotes devolatilisation, aromatic condensation, and structural stability, but it can also decrease the abundance of oxygen-containing groups available for reactant adsorption, acid–base activity, or active-phase anchoring [57–60]. Lower temperatures may preserve these functionalities but produce less condensed carbon structures that are more susceptible to chemical alteration or loss of grafted species during catalyst reuse. Consequently, the optimum pyrolysis temperature cannot be selected from surface area or carbon content alone; it depends on whether the resulting biochar will function directly as a catalyst, as a support for an active phase, or as a precursor for subsequent functionalisation.

The catalytic consequences of this trade-off were demonstrated by Corrêa et al. (2023), who pyrolysed murumuru kernel shells at 450, 600, and 750 °C before subjecting the resulting biochars to the same sulfuric-acid functionalisation procedure. The sulfonated biochar prepared at 750 °C possessed a more condensed carbon framework, achieved an initial esterification conversion of 98.35%, and retained a conversion of 89.35% in the third reaction cycle. It also retained a greater proportion of its sulfur-containing groups after reuse than the material prepared at 450 °C [61]. These findings indicate that, in this system, the more condensed high-temperature carbon structure provided a more stable platform for retaining the grafted acidic functionality. The result should not be interpreted as evidence that higher pyrolysis temperatures are universally preferable because the optimum temperature remains dependent on the feedstock, functionalisation route, required surface chemistry, and reaction conditions.

2.3. *Interplay between biochar physicochemical properties and catalytic performance*

Biochar catalytic performance is governed by the synergistic interaction of its physicochemical properties rather than any individual characteristic in isolation. Feedstock composition and pyrolysis conditions influence the development of surface functional groups, mineral constituents, aromatic carbon structures, and pore architecture, which together determine the adsorption, activation, and transformation of reactant molecules. As a result, biochar's catalytic behaviour is best understood as the combined outcome of its structural and chemical evolution during thermochemical conversion [62,63].

Among the physicochemical attributes of biochar, surface functional groups and mineral constituents play a particularly important role in managing catalytic activity. Oxygen-containing functional groups, including hydroxyl (-OH), carboxyl (-COOH), carbonyl (-C=O), and phenolic (Ar-OH) species, contribute to the development of Brønsted acidic and basic sites while simultaneously enhancing the affinity of the carbon surface for polar reactants and supported catalytic species [64,65]. In parallel, inorganic constituents such as calcium, potassium, magnesium, and iron may remain embedded within the biochar matrix following pyrolysis, providing intrinsically active Lewis acidic or basic centres [66]. Together, these surface modifications and mineral species influence reactant adsorption, active-site formation, and catalyst-support interactions, thereby directly affecting the efficiency of esterification and transesterification reactions during biodiesel synthesis.

The aromatic carbon framework of biochar provides the structural foundation on which catalytic functionality develops. During pyrolysis, progressive carbonisation promotes the formation of condensed aromatic domains that enhance the thermal, chemical, and mechanical stability of the biochar matrix. Increased aromaticity is particularly beneficial in catalysis because it improves resistance to structural degradation under reaction conditions and strengthens interactions between the carbon support and deposited active species. The degree of aromatic condensation may influence electron transfer processes and the distribution of surface-active sites, thereby affecting catalytic performance. Aromaticity represents an important parameter governing both catalyst durability and long-term reactivity in biodiesel production systems [67–69].

Within this physicochemical framework, pore architecture determines whether chemically active regions are accessible to the reactants. In FAME production, interconnected mesopores and macropores facilitate the transport of bulky triglycerides and FFAs, meaning that a high measured surface area is beneficial only when the relevant active sites can be reached and effectively utilised [70]. The optimisation of pore structure contributes not only to enhanced reactant interaction but also to improved mass transfer, catalyst utilisation, and overall reaction efficiency.

The relative contributions of these properties are difficult to distinguish when catalysts are compared across unrelated studies. More

informative evidence is obtained when feedstock, modification, or activation is varied within the same experimental investigation. The selected studies summarised in Table 2 provide a comparative overview of how biochar feedstock, thermal preparation, functionalisation and reaction conditions influence catalytic performance and reuse behaviour. The table includes acid-, base- and bifunctional systems to reflect the principal catalyst classes discussed in this review.

Table 2 consolidates representative studies reporting the biochar feedstock, preparation and functionalisation approach, catalyst loading, reaction conditions, biodiesel performance and reusability. The selected studies illustrate the diversity of biochar-based catalyst designs and reaction systems; however, differences in feedstock composition, catalyst preparation, heating method and performance reporting prevent direct numerical ranking across the studies.

The comparison by Behera et al. demonstrates that BET surface area alone is not an adequate predictor of catalytic performance. Although the selected peanut-shell catalyst had a surface area of only 6.616 $m^2\ g^{-1}$, its sulfonic-acid functionality enabled a biodiesel yield of 94.91% under the optimised conditions [71]. This does not establish that low surface area is generally advantageous; instead, it indicates that the accessibility and chemical activity of the available sites can be more important than total measured area. The influence of feedstock cannot be separated completely from the resulting pore structure, carbon framework, mineral composition, and response to functionalisation.

The results of Zubair et al. similarly show that modification can substantially alter catalytic performance even when the carbon precursor remains unchanged. The increase in biodiesel yield from 47.54% for the unmodified biochar to 98.96% for the KOH-modified material reflects the combined effects of changes in porosity and surface chemistry. However, the decline to 80.37% after five cycles also indicates that high initial activity does not necessarily guarantee complete retention of performance [72]. Active-site stability, possible leaching, pore blockage, and regeneration behaviour must therefore be considered alongside initial biodiesel yield.

Comparisons among unrelated studies must nevertheless be interpreted cautiously. Reported biodiesel yields and FFA conversions are influenced by the lipid composition and initial FFA and water contents, as well as the alcohol-to-oil ratio, catalyst loading, temperature, reaction time, and analytical method. A higher yield reported for one biochar-based catalyst does not independently demonstrate that its support is superior. Reliable structure–performance conclusions require controlled comparisons in which a specific synthesis or catalyst variable is changed while the reaction system is kept constant, together with adequate reporting of pore characteristics, active-site density, reaction conditions, and reuse performance.

2.4. Active sites and surface functionality in biochar catalysts

Catalytically active sites in biochar-based materials may originate from oxygen- or heteroatom-containing functional groups, retained inorganic species, structural defects, and persistent free radicals generated during thermochemical conversion. Their abundance and chemical nature depend on feedstock composition, pyrolysis conditions, and subsequent functionalisation [76]. Surface functionalities may participate directly in catalysis or provide anchoring sites for supported metals and metal oxides. Their composition and chemical states are commonly evaluated using techniques such as Fourier-transform infrared spectroscopy and X-ray photoelectron spectroscopy, while acid–base titration and temperature-programmed desorption can provide complementary information on active-site density and strength [77,78].

Oxygen-containing groups such as carboxylic, phenolic, carbonyl, and lactone functionalities contribute to surface acidity, reactant adsorption, and interactions with deposited active phases. Sulfonic-acid groups provide strong Brønsted acidity for FFA esterification, whereas nitrogen-containing groups, including pyridinic and pyrrolic nitrogen, can increase electron density and surface basicity. Retained or introduced alkali and alkaline-earth species may provide Lewis-basic centres that promote methoxide formation during transesterification. The principal active-site classes and their catalytic roles are summarised in Table 3 [79–81].

The abundance and distribution of active centres on biochar surfaces are strongly influenced by the conditions employed during thermochemical conversion. Variations in pyrolysis temperature, residence time, and reaction atmosphere can alter the concentration and availability of acidic and basic functions, thereby influencing catalytic behaviour. Conditions that favour the preservation of oxygen-containing groups may enhance Brønsted acidity. In contrast, more severe thermal treatments often promote the development of highly condensed aromatic structures with fewer surface functionalities. The catalytic significance of these surface functional groups has been demonstrated across numerous biodiesel studies. Brønsted acidic groups, particularly surface-grafted $–SO_3H$ functions, are widely recognised as the principal active sites governing esterification, while oxygen-containing groups such as –COOH and phenolic –OH contribute to surface acidity and

Table 2
Selected comparisons demonstrating relationships between carbon-support properties and catalytic performance in biodiesel production [71–75].

Study	Biochar feedstock	Preparation conditions and functionalisation	Catalyst loading and reaction conditions	Biodiesel yield or conversion	Reusability
Behera et al. (2020)	Sugarcane bagasse, coconut shell, corncob and peanut shell; peanut-shell biochar selected as the best-performing material	Biomass pyrolysed at different temperatures and surface-functionalised with sulfonic acid groups; the selected peanut-shell biochar was produced at 400 °C and had an acid-site density of 0.837 mmol g^{-1}	Algal oil; 5 wt. % catalyst; methanol:oil ratio of 20:1; 65 °C; 4 h	94.91% biodiesel yield; reported FAME content of 59.73%	Not reported
Zubair et al. (2023)	Marine macroalgae	Biochar prepared by slow pyrolysis and subsequently activated using KOH; unmodified biochar and KOH-modified activated carbon were compared	Waste cooking oil; 3.08 wt. % catalyst; methanol:oil ratio of 12.3:1; 66 °C; 130 min	47.54% for unmodified biochar and 98.96 % for KOH-modified biochar	KOH-modified catalyst retained an 80.37% yield after five cycles
Foroutan et al. (2021)	Brown alga, *sargassum oligocystum*	Algal biomass pyrolysed at 350 °c for 120 min; biochar combined with eggshell-derived CaO and K_2CO_3	Waste edible oil; 4 wt% catalyst; methanol:oil ratio of 18:1; 65 °C; 200 min	98.83%	Approximately 90% efficiency after five cycles
Yadav et al. (2023)	Bamboo and coconut-husk wastes	Dual-feedstock biochar prepared through H_3PO_4assisted carbonisation and subsequently functionalised with sulfonic acid groups using H_2SO_4	Oleic acid; 3 wt.% catalyst; methanol:oleic acid ratio of 9:1; 80 °C; 40 min under microwave irradiation	99.6 ± 0.4%	Effective for up to six cycles
Ñanculeo et al. (2025)	Oat hulls	Biomass impregnated with KOH at an optimum KOH:biomass mass ratio of 2:1 and pyrolysed at 600 °C for 3 h under N_2	Waste cooking oil; 2.5 wt. % catalyst; methanol:oil ratio of 12:1; 150 °C; 1 min under microwave irradiation	100 % FAME	Evaluated for three cycles; washing between cycles substantially improved activity retention

Table 3
Principal active-site classes in biochar-based catalysts and their functions in biodiesel production.

Active-site class	Representative examples	Principal catalytic function
Brønsted-acidic sites	-COOH, SO_3H, lactone, phenolic	Protonation of fatty-acid carbonyl groups during esterification and enhancement of polar-reactant adsorption.
Lewis-acidic sites	Supported metal cations and coordinatively unsaturated metal or metal-oxide centres.	Polarisation and activation of carbonyl groups and interaction with oxygen-containing reactants.
Brønsted- or Lewis-basic sites	Nitrogen-containing groups and accessible Na-, K-, Ca- or Mg-containing species.	Alcohol activation and methoxide formation during triglyceride transesterification.
Anchoring and adsorption sites	Carbonyl, hydroxyl, ether and defect sites within the carbon framework.	Immobilisation and dispersion of supported active phases and adsorption of reactant molecules.
Electronically active sites	Persistent free radicals, structural defects and conjugated aromatic domains.	Electron transfer and charge redistribution; their importance depends on the catalytic reaction and active phase.

improve reactant adsorption [82,83]. For example, Yang et al. reported that chlorosulfonic acid-functionalised *Camellia oleifera* shell biochar exhibited an acid density of 2.86 mmol g^{-1}, achieving a biodiesel yield of 91.4% while retaining approximately 90% of its catalytic activity after four reuse cycles. These findings demonstrate how appropriate control of synthesis conditions and subsequent surface functionalisation can increase the density of accessible Brønsted acid sites and translate directly into improved catalytic activity [84].

Beyond conventional surface functionalities, persistent free radicals (PFRs) and mineral-derived active centres can contribute significantly to biochar reaction behaviour. PFRs originate during thermochemical conversion and create electronically active regions that facilitate electron transfer and promote redox reactions. Inorganic minerals can participate directly in catalytic transformations or enhance interactions between biochar and deposited active phases [85]. As a result, both PFRs and mineral-derived active sites contribute to biochar's catalytic functionality, expanding its applicability across a range of catalytic processes, including biodiesel production.

The diverse active centres present on biochar surfaces govern its reaction behaviour by influencing reactant interaction, acid-base behaviour, electron transfer and catalyst-support interactions. Biomass, thermochemical conversion conditions, and subsequent modification strategies determine the relative abundance and distribution of these sites. Understanding the nature of these active sites is fundamental for the rational design of biochar-based catalysts and catalyst supports for FAME production.

Fig. 5 schematically illustrates the diverse active areas on biochar surfaces. These include oxygen-containing groups, heteroatom-containing groups, persistent free radicals, and mineral-derived active centres that contribute to the catalytic behaviour of biochar-based catalysts.

2.5. Functionalisation strategies for biochar-based catalysts

Although pristine biochar has inherent catalytic activity due to its surface functionality, mineral composition, and porous structure, its performance is often insufficient for demanding catalytic conversions. Functionalisation strategies tailor the physicochemical attributes and active-site distribution of biochar, thereby enhancing catalytic performance. Through acid treatment, alkaline activation, metal incorporation, and heteroatom doping, biochar can be engineered to demonstrate increased acidity, basicity, redox activity, and catalyst stability. These modifications enable the rational design of biochar-based catalysts and

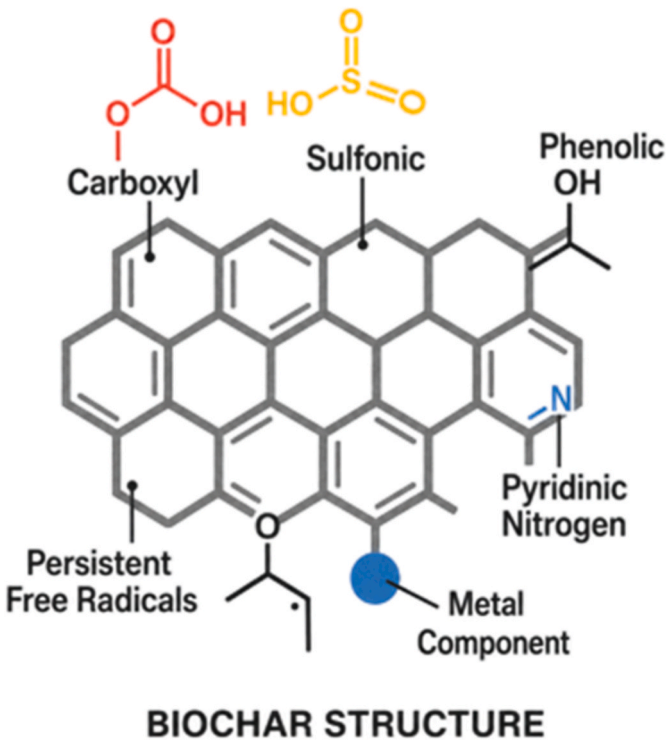


Fig. 5. Representative schematic illustrating the principal oxygen-containing, sulfur-containing, nitrogen-containing, mineral-derived, and electronically active sites.

catalyst supports for biodiesel conversion from both high- and low-FFA feedstocks.

Activation should be distinguished from functionalisation because its primary purpose is to develop or modify the pore network, although it may also alter surface chemistry and mineral composition. Physical activation commonly employs steam or CO_2 to promote controlled gasification of the carbon framework, whereas chemical activation uses agents such as KOH, H_3PO_4, or $ZnCl_2$ to facilitate pore development. The resulting properties depend on the activating agent, activating-agent-to-biochar ratio, treatment temperature, residence time, and washing procedure. Increasing activation severity can increase surface area and pore volume, but excessive treatment may widen or collapse pores, decrease carbon yield, remove oxygen-containing anchoring groups, or weaken the carbon framework. Residual activating species may additionally contribute to apparent acid–base activity or promote leaching if they are not adequately removed [86,87].

For biodiesel catalysis, activation should therefore be optimised according to accessible pore structure and active-site utilisation rather than maximum BET surface area alone. Micropore formation may substantially increase measured surface area without improving the transport of bulky triglycerides, whereas mesopore and macropore development can improve access to supported or grafted catalytic sites. Activation can also affect the dispersion and retention of an active phase by changing surface roughness, functional-group abundance, and pore dimensions. Chang et al. (2025), for example, reported that KOH activation of sunflower-straw-derived biochar produced a material with a surface area of 1032 m^2 g^{-1} and altered its porosity, aromaticity, and graphitic character [88]. These structural improvements may benefit catalyst-support applications, but catalytic performance must still be confirmed directly because activation simultaneously changes several material properties.

2.5.1. Acid functionalisation

The acid functionalisation of biochar involves the introduction of

Brønsted-acidic groups, including sulfonic (–SO_3H), carboxylic (–COOH), and phenolic (–OH) groups, along with other oxygen-containing surface functionalities that promote the protonation of free fatty acids and facilitate esterification. Among the available modification strategies, sulfonation is the most widely employed and effective approach for producing solid-acid biochar catalysts. This is typically achieved using concentrated sulfuric acid, chlorosulfonic acid, or *p*-toluenesulfonic acid, thereby grafting surface-bound –SO_3H groups that substantially increase Brønsted acidity and the density of accessible acid sites. Sulfonated biochars generally exhibit superior catalytic activity and stability during esterification and, under appropriate conditions, transesterification reactions. In contrast, weaker organic acids such as citric, acetic, and tartaric acids have also been explored for surface modification but typically generate lower acid-site densities. The effectiveness of acid-functionalised biochar ultimately depends on the density, accessibility, and stability of the introduced acidic groups, as well as the carbon framework's ability to retain these functionalities during repeated reaction cycles. Lower pyrolysis temperatures, typically between 350 and 500 °C, are generally more favourable for preserving oxygen-containing surface groups that serve as precursors for subsequent acid functionalisation [82,89,90].

The catalytic benefits of acid functionalisation have been demonstrated in several biodiesel studies. Cao et al. (2023) reported that sulfonated corncob-derived biochar revealed a -SO_3H density of 2.05 mmol/g and achieved an oleic acid conversion efficiency of 98.5%, highlighting the effectiveness of sulfonic acid groups in promoting esterification reactions [91]. Similarly, Rashid et al. (2019) observed that sulfonation of tea-waste-derived biochar increased both surface area and acid-site density, resulting in a 97% conversion of free fatty acids during the esterification of palm fatty acid distillate [92]. The introduction of strong Brønsted acidic functionalities significantly enhances catalytic performance in biodiesel production systems.

Beyond FAME production, the advantages of acid functionalisation have also been demonstrated through improvements in surface reactivity and functional-group density. Lonappan et al. (2020) reported that organic acid modification increased the abundance of acidic surface chemistry in several biochars, with citric acid proving particularly effective at enhancing carboxylic group incorporation. This improved surface chemistry enhanced adsorption performance, highlighting the broader role of acid functionalisation in tailoring biochar reactivity and active-site accessibility [93].

These studies show that acid functionalisation enhances biochar catalytic activity by increasing the density of accessible Brønsted acid sites and improving reactant activation during esterification. Sulfonated biochars have consistently exhibited high FFA conversion efficiencies owing to the strong acidity of surface bound SO_3H groups. The effectiveness of acid-functionalised biochar is governed not only by the presence of acidic functionalities but also by their stability, accessibility, and interaction with the underlying carbon framework.

2.5.2. *Base functionalisation*

In contrast, base functionalisation enhances biochar catalytic activity in transesterification, in which triglycerides are converted into fatty acid methyl esters (FAMEs). This process relies on surface basicity to generate methoxide ions from methanol, which then act as nucleophiles in triglyceride conversion. Basic functionalities are commonly generated by incorporating alkaline metal species, including potassium-, calcium-, and sodium-based compounds, which create Lewis basic centres on the biochar surface. These active sites facilitate methoxide ion formation and promote nucleophilic attack on triglycerides, thereby accelerating transesterification reactions. The effectiveness of base-functionalised biochars is strongly influenced by the density, accessibility, and stability of these basic sites, as well as their interactions with the porous carbon framework [94–96]. Although highly active, such catalysts are generally more sensitive to moisture and high FFA contents, which may result in saponification, active-site leaching or catalyst deactivation under certain reaction conditions.

The catalytic benefits of base functionalisation have also been demonstrated in biodiesel production applications. Ribeiro et al. (2023) developed a sodium-modified biochar catalyst (15Na/BCAM) for the transesterification of soybean oil, achieving an ester content of 97.2%. The catalyst remained catalytically active over five consecutive reaction cycles, although the ester content decreased from its initial value and remained above 65% after five cycles [97]. These findings demonstrate that sodium incorporation generated basic sites capable of promoting biodiesel synthesis, while the decline during reuse highlights the continuing importance of active-site retention and catalyst regeneration.

The available studies consistently show that the base functionalisation enhances biochar catalytic performance by increasing the density of accessible Lewis basic sites and promoting methoxide generation during transesterification. Alkaline-modified biochar exhibits high catalytic activity and can achieve excellent biodiesel yields when active-site accessibility and catalyst stability are appropriately optimised [98,99]. However, their susceptibility to moisture, FFAs, and active-site leaching remains an important consideration for practical applications. The successful implementation of base-functionalised biochar catalysts requires a balance between catalytic activity, stability, and resistance to deactivation under operating conditions.

The preceding discussion describes how feedstock selection, pyrolysis, activation, and functionalisation determine the properties of biochar-based catalysts and catalyst supports. Fig. 6 integrates these preparation stages with their subsequent application in biodiesel production, catalyst recovery, deactivation, regeneration, and end-of-life management, thereby providing a lifecycle framework for the discussions that follow.

3. Catalytic behaviour of biochar in esterification and transesterification reactions

The catalytic behaviour of biochar in biodiesel production is

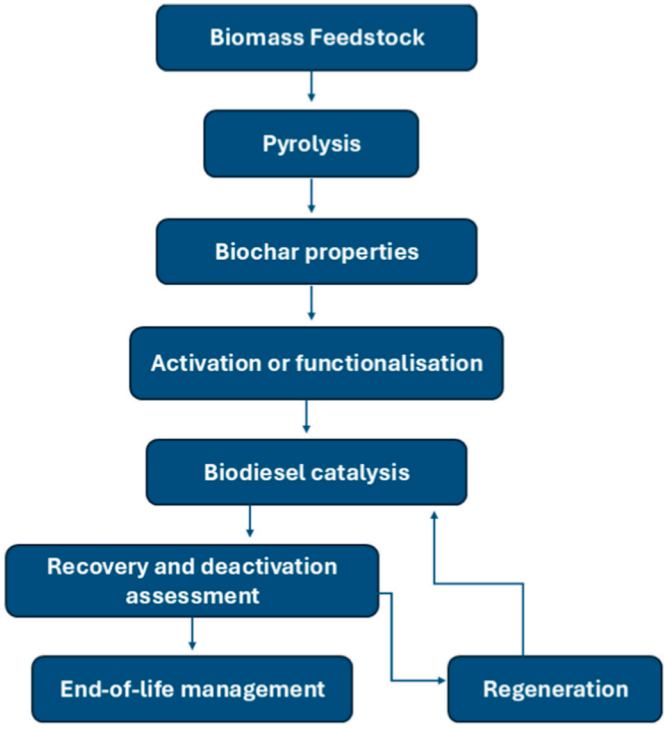


Fig. 6. Lifecycle of biochar-based catalysts and catalyst supports for biodiesel production, from biomass selection and pyrolysis to modification, catalysis, regeneration, reuse, and end-of-life management. Carbon retention depends on the stability and appropriate management of the spent catalyst.

intrinsically linked to its surface chemistry, porosity, and functional group distribution. Although structural and chemical modifications of biochar enhance its potential as a solid catalyst, its practical applicability depends on its performance in specific reactions, particularly esterification and transesterification [100]. These two reactions constitute the core pathways for biodiesel synthesis and require distinct active sites and catalyst environments.

Esterification and transesterification require chemically distinct catalytic functions. Acid-functionalised biochars containing Brønsted-acidic groups, particularly –SO_3H and –COOH, promote the esterification of free fatty acids with alcohol to form FAMEs and are therefore suitable for high-FFA feedstocks. In contrast, base-functionalised biochars containing accessible alkali, alkaline-earth, or metal-oxide species promote methoxide formation and the transesterification of triglycerides into FAMEs and glycerol. These base catalysts are generally most effective with feedstocks containing low concentrations of FFAs and water because FFAs can neutralise basic sites and promote saponification. Feedstocks containing substantial quantities of both FFAs and triglycerides may instead require sequential acid–base treatment or a bifunctional catalyst capable of facilitating both reactions within the same process [101].

The following sections examine how biochar performs under esterification and transesterification conditions, with a particular focus on catalytic activity, conversion efficiency, operating conditions, and long-term reusability. By exploring the interaction between biochar's surface chemistry and reaction kinetics, these sections aim to clarify the catalytic behaviour and potential of the biochar-based catalysts as sustainable alternatives for FAME production.

3.1. Catalytic behaviour of biochar in esterification

Esterification is a crucial step in biodiesel production, particularly when processing low-quality or waste feedstocks that contain high levels of free fatty acids (FFAs). In this reaction, FFAs are converted into FAMEs in the presence of an alcohol, typically methanol, and an acid catalyst, as seen in Fig. 7. FFAs in feedstocks are problematic for base-catalysed transesterification because they lead to soap formation and catalyst deactivation. As a result, esterification is commonly used as a pretreatment step, and solid acid catalysts, such as functionalised biochar, offer a sustainable and reusable alternative to homogeneous acids such as sulfuric acid [102,103].

The efficiency of biochar-based catalysts in esterification depends heavily on acid-site density, functional-group thermal stability, and active-site accessibility. Lim et al. (2020) developed a sulfonated biochar catalyst from oil palm empty fruit bunch using 4-benzenediazonium sulfonate (4-BDS) as a sulfonating agent. Characterisation confirmed the successful incorporation of sulfonic acid groups and the catalyst's good thermal stability. Under optimal preparation conditions, involving calcination at 200 °C and a sulfanilic acid-to-carbon ratio of 15:1, the catalyst achieved a biodiesel yield of 98.1% after 7 h using a catalyst loading of 20 wt.%. The high yield was attributed to the introduced sulfonic-acid functionality and the developed porous carbon surface [104].

In addition to initial catalytic activity, catalyst reusability is an important consideration for practical esterification processes. Yusuff et al. (2022) evaluated an oxygen-rich biochar derived from eucalyptus bark and functionalised with p-toluenesulfonic acid (p-TSA). The resulting catalyst possessed an acid-site density of 468.8 μmol g^{-1} and achieved a FAME yield of 97.05% at 65 °C within 2 h using a methanol-to-oleic-acid molar ratio of 10:1 and a catalyst loading of 4 wt.%. The catalyst was reused over five successive cycles without a dramatic decline in catalytic performance [105]. However, FTIR analysis of the spent catalyst showed decreased bands associated with –SO_3H groups, while EDX revealed a lower sulfur content than in the fresh catalyst, suggesting partial loss of acidic species during reuse. The retained FAME yield therefore demonstrates operational reusability, but it does not establish that the introduced acid sites remained chemically unchanged.

These studies demonstrate that acid-functionalised biochar catalysts can achieve high esterification efficiencies under optimised conditions. However, initial FAME yield, reuse performance, and direct evidence of active-site stability should be reported as distinct measures. Repeated catalytic activity provides evidence of operational reusability, whereas confirmation of catalyst stability additionally requires evaluation of active-species leaching, activity of the separated liquid phase, and changes in the chemical or structural properties of the recovered catalyst. Accordingly, the available results support the potential of biochar-based solid acids for high-FFA feedstocks, but claims of long-term stability should be reserved for studies providing direct evidence of active-site retention.

3.2. Catalytic behaviour of biochar in transesterification

Transesterification is the primary reaction pathway for converting triglyceride-rich feedstocks into FAMEs, and base-functionalised biochar catalysts have attracted significant attention for their reusability, ease of separation, and solid-phase handling. These catalysts generate methoxide ions from alcohol, which are crucial for nucleophilic attack on triglyceride carbonyl groups. Reaction efficiency depends on the strength and availability of the basic sites, catalyst porosity, and the catalyst's resistance to deactivation [106]. Fig. 8 illustrates the proposed sequence of methanol adsorption, methoxide-ion formation, nucleophilic attack on the triglyceride carbonyl group, FAME formation, and regeneration of the basic active site.

The catalytic performance of biochar-supported base catalysts has been demonstrated using several waste-derived materials. Das et al. (2022) prepared a catalyst from calcined waste-eggshell-derived CaO combined with lanthanum and switchgrass biochar and applied it to the transesterification of lipids obtained from *Desmodesmus maximus*. The optimised catalyst produced a biodiesel conversion of 99%. During reuse, conversion progressively decreased to 77% in the tenth reaction cycle [107]. These results demonstrate substantial operational reusability over ten cycles, but the decrease in conversion also indicates progressive catalyst deactivation. Without direct analysis of calcium or lanthanum leaching, liquid-phase activity, or the chemical composition of the recovered catalyst, the reuse data should not be interpreted independently as proof that the supported basic sites remained unchanged.

Beyond CaO-based systems, Li et al. (2024) prepared an oak-leaf-derived biochar/Fe_3O_4–CuO nanocatalyst for the ultrasonic-assisted transesterification of *Annona reticulata* oil. Under the optimised

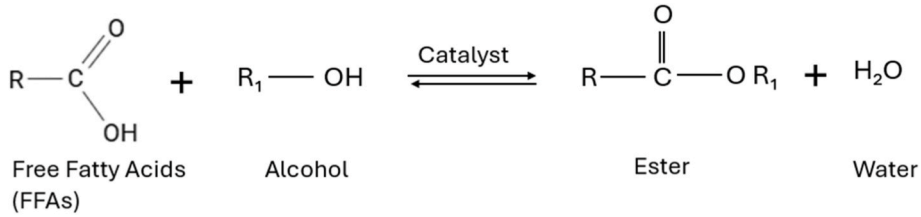


Fig. 7. Acid-catalysed esterification mechanism illustrating the conversion of free fatty acids (FFAs) into fatty acid methyl esters (FAMEs).

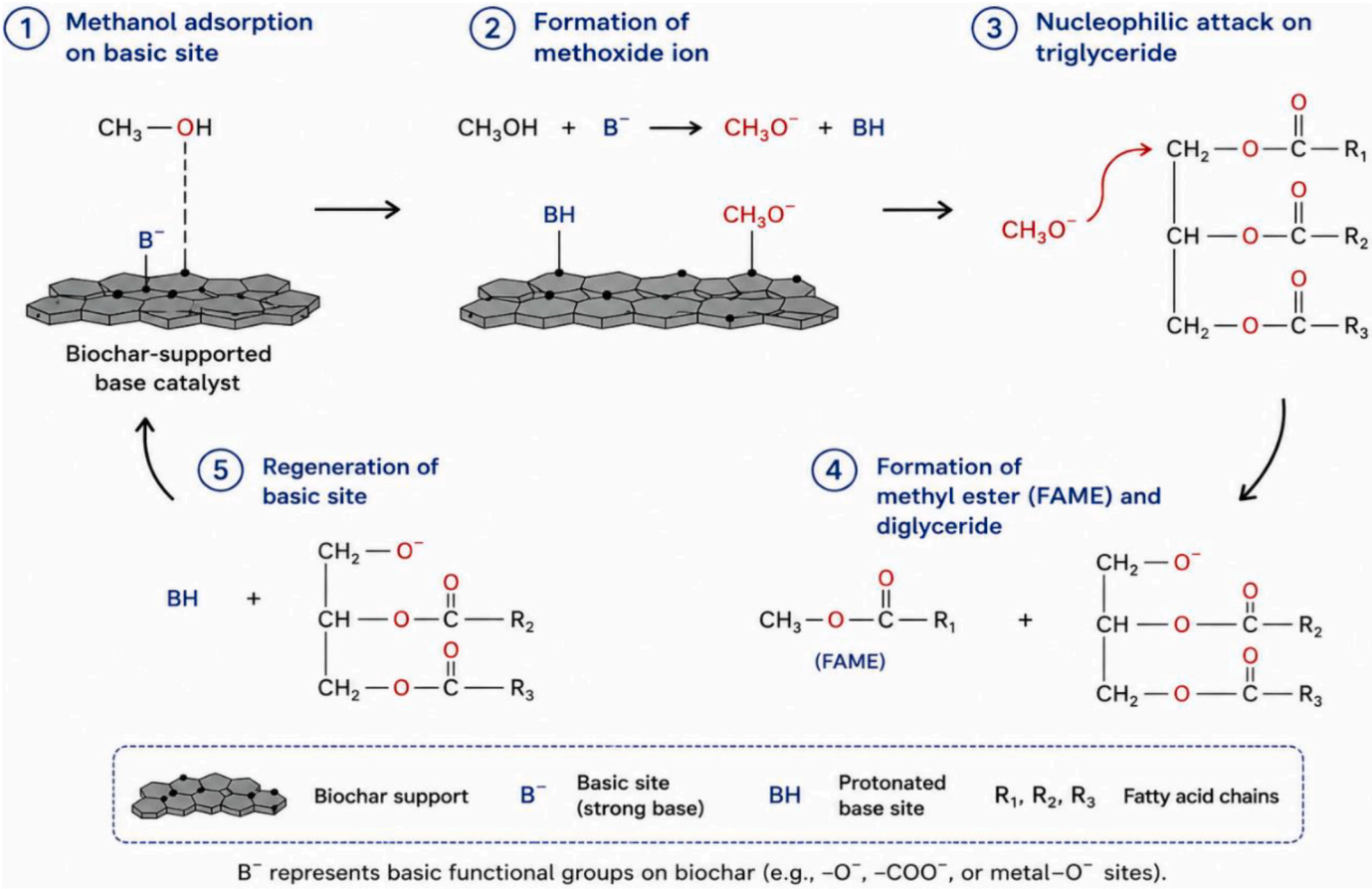


Fig. 8. Proposed base-catalysed transesterification mechanism over a biochar-supported catalyst.

conditions of a methanol-to-oil ratio of 12.2:1, a catalyst loading of 2.13 wt.%, and a temperature of 65 °C, a biodiesel yield of 97.9% was achieved within 30 min [108]. The magnetic component facilitated catalyst recovery, and the catalyst was evaluated over seven reuse cycles with high retained catalytic performance. These results support the operational recoverability and reusability of the composite; however, magnetic recovery and retained yield do not by themselves establish that CuO or other catalytically active species did not leach during reaction.

Across the studies examined, biochar-supported base catalysts achieved high initial transesterification activity and remained catalytically active over multiple reuse cycles [109–111]. Nevertheless, a decline in biodiesel yield or conversion during repeated operation indicates progressive deactivation, which may result from active-species leaching, pore blockage, surface carbonation, hydration of basic oxides, or structural changes in the supported phase. Reuse tests should therefore be interpreted as evidence of operational reusability, whereas claims of active-site stability require additional evidence from leaching measurements, filtrate-activity tests, or characterisation of the recovered catalyst. The practical performance of base-functionalised biochars consequently depends on both high initial basic activity and resistance to chemical and structural deactivation under transesterification conditions.

3.3. *Bifunctional biochar catalysts for simultaneous esterification and transesterification*

Bifunctional biochar-based catalysts contain acidic sites that promote FFA esterification and basic sites that facilitate triglyceride transesterification. Typical acidic functionalities include –SO_3H and –COOH groups, whereas the basic component commonly comprises CaO, ZnO, K-containing species, or other metal oxides [112]. Combining these functions within one catalyst can enable the processing of lipid feedstocks containing both FFAs and triglycerides without a separate acid-pretreatment stage. This approach is particularly relevant to waste cooking oil, tallow, soapstock, and other low-quality feedstocks, although effective operation requires both types of sites to remain accessible and chemically active under the same reaction conditions.

Feng et al. developed a ZnO/PVP-mediated sulfonated insect-shell biochar catalyst in which the sulfonated carbon supplied acidic functionality and ZnO provided basic sites. Importantly, spent-catalyst characterisation revealed reduced ZnO peak intensity and glycerol-associated surface groups, indicating that active-component loss and site blockage contributed to deactivation (Table 4) [113].

Recent composite catalysts further demonstrate the different strategies used to combine acid and base functions. Xia et al. prepared a magnetic CoFe/biochar/CaO catalyst in which CoFe contributed acidic functionality and magnetic recoverability, while CaO provided basic sites. The catalyst achieved an initial biodiesel yield of 99.21% from waste cooking oil and retained a yield of 91.70% in the fifth cycle. Characterisation indicated that interaction between the biochar support and the Ca-containing phase reduced, but did not necessarily eliminate, active-component loss [114]. Derbe et al. (2024) instead combined zeolite-A with biochar and obtained a maximum yield of 86.22%, compared with 69.42% for zeolite-A and 74.27% for biochar individually. The composite remained catalytically active over five cycles, although the non-monotonic reuse results and decline in yield indicate that recyclability should not be interpreted as complete catalyst stability [115].

Osagiede and Aisien (2024) prepared a bifunctional catalyst by combining sulfonated rubber-seed-shell biochar with calcined eggshell.

Table 4
Representative bifunctional biochar-based catalysts for simultaneous esterification and transesterification in biodiesel production.

Study	Catalyst and proposed functions	Feedstock and initial performance	Reuse performance	Stability evidence and limitations
Feng et al. (2023)	ZnO/PVP-mediated sulfonated insect-shell biochar; sulfonated carbon provides acidic sites and ZnO supplies basic functionality	Insect lipid; 94.36% biodiesel yield	Evaluated for five cycles; second-cycle yield was 88.66%, followed by a gradual decline.	Spent SEM, TEM, XRD and FTIR were reported. Reduced ZnO peak intensity indicated active-component loss, while glycerol-associated bands suggested site blockage.
Xia et al. (2024)	Magnetic CoFe/biochar/CaO; CoFe provides acidic functionality and magnetic recovery, while CaO supplies basic sitesCoFe-BC/CaO	Waste cooking oil; 99.21% biodiesel yield	91.70% yield after the fifth cycle	Characterisation indicated strong anchoring of nanoscale Ca-containing species on the biochar, which reduced CaO loss. Direct quantitative leaching results should still be reported where available.
Derbe et al. (2024)	Zeolite-A/biochar composite	Waste cooking oil; 86.22% yield, compared with 69.42% for zeolite-A and 74.27% for biochar	82.98, 79.08, 62.87 and 76.84% in cycles 2–5, respectively	Reuse was demonstrated, but the non-monotonic performance and fourth-cycle decline prevent a strong claim of complete stability without supporting leaching or spent-catalyst evidence.
Osagiede et al. (2024)	Sulfonated rubber-seed-shell biochar/calcined eggshell; acidic sulfonated carbon and basic eggshell-derived CaO	Waste cooking oil; 89.4% optimum biodiesel yield and 91.6% FFA conversion	81.9% biodiesel yield after the fifth cycle	Insignificant catalyst leaching was reported. Initial and fifth-cycle yields must nevertheless be treated as separate performance measures.

The sulfonated biochar supplied acidic sites for FFA esterification, whereas the eggshell-derived CaO provided basic sites for triglyceride transesterification. Under the optimised conditions, the catalyst achieved a biodiesel yield of 89.4% and an FFA conversion of 91.6%. The biodiesel yield after the fifth cycle was 81.9%, which should be reported separately from the optimum initial performance. The authors additionally reported insignificant catalyst leaching, providing stronger evidence of heterogeneity than reuse results alone [116]. Representative performance and stability evidence for these bifunctional systems are compared in Table 4.

The principal challenge in bifunctional catalyst design is not simply maximising the total quantities of acidic and basic sites. If the two functions are located too closely, acid–base neutralisation may reduce the number of catalytically available sites. Conversely, excessive separation may restrict the sequential transport of FFAs, triglycerides, and intermediate products between the two catalytic environments. High active-phase loading can increase nominal site density but may also block pores, promote metal-oxide agglomeration, and restrict access of bulky lipid molecules. Effective bifunctional catalysts therefore require an appropriate balance among acid–base site density, spatial distribution, pore connectivity, and reactant accessibility.

Stability is particularly challenging because the two catalytic functions may respond differently to the reaction environment. Water formed during FFA esterification can hydrate or deactivate basic oxides, while FFAs may neutralise accessible basic sites before esterification is complete. CaO-, ZnO-, and alkali-containing phases may also leach into the methanol–oil reaction mixture, whereas sulfonic-acid groups can be lost through hydrolysis or weak attachment to the carbon framework. Stronger anchoring of the active phases and partial spatial separation of acidic and basic domains may reduce these interactions, but such claims should be supported by leaching analysis, filtrate-activity tests, and characterisation of the spent catalyst.

The studies in Table 4 [113–116] demonstrate that high initial biodiesel yields can be achieved using several bifunctional architectures, but they also reveal different levels of stability evidence. Reuse testing alone demonstrates operational recyclability; Feng et al. additionally characterised the spent catalyst and identified ZnO loss and surface blockage, while Osagiede and Aisien reported a leaching assessment. Future bifunctional-catalyst studies should quantify acidic and basic site densities separately, determine whether both functions remain accessible after reaction, and report initial yield, retained yield, active-species leaching, and changes in the recovered catalyst as distinct performance indicators.

3.4. Catalytic properties and comparative performance

The catalytic performance of biochar-based catalysts in biodiesel synthesis is governed by the interplay of several physicochemical properties rather than by a single material characteristic. While acidic surface functionalities promote esterification and basic active sites facilitate transesterification, catalytic efficiency also depends on factors such as pore accessibility, surface area, catalyst stability, and the availability of accessible active sites. These properties collectively influence reactant diffusion, active-site utilisation, product formation, and catalyst durability under reaction conditions [117]. Consequently, understanding the relationship between these physicochemical characteristics and catalytic behaviour is essential for the rational design and optimisation of biochar-based catalysts for FAME production.

Efficient biodiesel production relies on catalysts possessing a combination of physicochemical properties that promote high catalytic activity, selectivity, and long-term operational stability. Fig. 9 summarises four characteristics that influence the performance of biochar-based

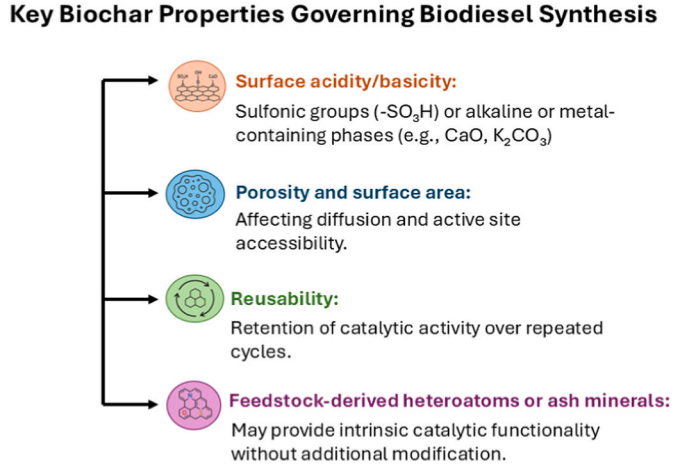


Fig. 9. Key functional properties of biochar-based catalysts for biodiesel synthesis.

catalysts: surface acidity or basicity, pore architecture and surface area, catalyst reusability, and the contribution of feedstock-derived heteroatoms or mineral species. Together, these features govern reactant conversion, active-site utilisation, and sustained catalytic operation [118].

Quantitative structure–performance comparisons remain challenging because biochar-based catalysts are characterised and tested using different methods, lipid feedstocks, and reaction conditions. Nevertheless, selected high-performing acid-functionalised biochars provide useful performance ranges for evaluating the relative importance of acid-site density and pore structure. Table 5 compares studies reporting biodiesel yields or conversions above 90% together with available acidity and textural data. Missing values are retained as "not reported" because estimating them would create unsupported structure–performance relationships.

Among the selected acid-functionalised catalysts, biodiesel yields above 90% were reported across acid-density values ranging from 0.4688 to 3.2 mmol g^{-1}. Within the selected high-performing studies, approximately 0.47 mmol g^{-1} was the lowest reported total acidity. This value may therefore serve as a literature-derived reference point for experimental screening, but it should not be interpreted as a universal performance threshold. Acid density was measured using different procedures, and the fraction of sites that were accessible and catalytically active was not quantified consistently. Furthermore, the higher-acidity materials did not necessarily provide higher yields, demonstrating that total acid density alone is insufficient to predict catalytic performance.

The textural properties varied even more widely. Catalysts producing yields above 90% possessed BET surface areas ranging from 2.67 to 1196.13 m^2 g^{-1} and reported average pore dimensions ranging from 4.12 to 108.77 nm. Yusuff et al. achieved 97.05% FAME yield with a total pore volume of 0.24 cm^3 g^{-1}, but comparable pore-volume values were not reported for most of the other catalysts. Consequently, the available data do not support a defensible minimum mesopore-volume threshold. The results instead indicate that sufficiently open pores capable of admitting lipid molecules and exposing the relevant acid sites are more important than maximising total surface area or pore volume. The high performance of materials with surface areas below 10 m^2 g^{-1} further confirms that BET area alone is not an appropriate design criterion.

Based on the available evidence, three provisional design rules can be identified. First, an acid density of approximately 0.47 mmol g^{-1} or greater represents a reasonable initial screening target for sulfonated biochars, provided that the acidic sites are accessible and strongly retained. Second, the pore network should contain mesopores or larger transport pathways rather than being dominated by inaccessible microporosity. Third, initial yield must be evaluated together with acid-site retention, leaching, and pore accessibility after reuse. These rules define experimentally observed performance conditions rather than universal thresholds, because differences in feedstock composition, alcohol ratio, catalyst loading, temperature, reaction time, and analytical method prevent direct causal comparison among the reported studies.

4. Catalyst longevity and regeneration

The practical viability of biochar-based catalysts extends beyond their initial catalytic activity and biodiesel conversion efficiency. For industrial applications, catalysts must retain their physicochemical properties, active-site accessibility, and catalytic performance over repeated reaction cycles while remaining amenable to effective regeneration. Catalyst longevity and recovery are critical considerations for evaluating the long-term feasibility of biochar-based catalysts in biodiesel production. During operation, biochar catalysts may undergo physicochemical changes that reduce active-site availability, alter structural properties, or diminish catalytic activity, leading to progressive performance losses. Consequently, understanding the mechanisms responsible for catalyst deactivation and the effectiveness of regeneration strategies is essential to improve catalyst durability, reduce operational costs, and support the large-scale implementation of sustainable FAME production [121–123].

4.1. Deactivation mechanisms in biochar-based catalysts

Despite their promising catalytic performance, biochar-based catalysts gradually lose activity during repeated biodiesel production cycles, owing to changes in their physicochemical properties and active-site availability. The extent of catalyst degradation depends on factors such as reaction conditions, feedstock composition, catalyst structure, and the stability of the incorporated active species. Catalyst deactivation generally occurs through four principal mechanisms, each affecting catalyst behaviour differently [124–126].

- **Coking and pore blockage:** Carbonaceous deposits originating from triglycerides, FFAs, glycerol, soaps or reaction intermediates may accumulate on the external surface and within the pore network. These deposits can cover catalytic sites, narrow or obstruct pore channels, restrict the diffusion of reactants and products, and progressively reduce catalytic activity. Pore blockage may also arise from retained feedstock impurities or large organic molecules, even when extensive coke formation has not been demonstrated.
- **Leaching and loss of active sites:** Surface-bound acidic functionalities, particularly -SO_3H groups, and incorporated basic species such as K-, Na- or Ca-containing phases may dissolve or detach

Table 5
Quantitative physicochemical properties and catalytic performance of selected acid-functionalised biochar catalysts [71,84,105,119,120].

Study and catalyst	Acidic functionality	Textural properties	Feedstock and reaction conditions	Performance
Yusuff et al. (2022), p-tsa$_3$/abc	Total acidity: 0.4688 mmol g^{-1}; –SO_3H-dominated surface acidity	BET area: 31 m^2 g^{-1}; total pore volume: 0.24 cm^3 g^{-1}; average pore diameter: 24.6 nm	Oleic acid; methanol-to-acid ratio 10:1; 4 wt.% catalyst; 65 °C; 2 h	97.05 ± 0.28% FAME yield
Behera et al. (2020), sulfonated peanut-shell biochar	–SO_3H density: 0.837 mmol g^{-1}	BET area: 6.616 m^2 g^{-1}; pore volume not reported	Algal oil; methanol-to-oil ratio 20:1; 5 wt.% catalyst; 65 °C; 4 h	94.91% biodiesel yield
Ao et al. (2024), 4-dbs-functionalised porous carbon	Sulfur functionality: 1.9 mmol g^{-1}; this value should not be treated as directly equivalent to titrated acid density	BET area: 1196.13 m^2 g^{-1}; average pore size: 4.12 nm	*Jatropha curcas* oil; methanol-to-oil ratio 22.9:1; 7.7 wt.% catalyst; 96.2 °C; 50.3 min	97.1 ± 0.4% biodiesel yield
Yang et al. (2024), sulfonated camellia oleifera shell biochar	Acid density: 2.86 mmol g^{-1}	BET area: 2.67 m^2 g^{-1}; pore volume not reported	Oleic acid; methanol-to-oleic-acid molar ratio of 6:1; 4 wt.% catalyst; 70 °C; 2 h.	91.4% biodiesel yield
Chellappan et al. (2023), dye-functionalised cassava-peel biochar	Total acid density: 3.2 mmol g^{-1}; –SO_3H density: 1.9 mmol g^{-1}	BET area: 4.89 m^2 g^{-1}; average pore width: 108.77 nm; pore volume not reported	*Millettia pinnata* seed oil; microwave-assisted reaction	91.25% biodiesel yield

during reaction, washing or catalyst recovery. Leaching reduces the active-site inventory and may introduce homogeneous catalytic contributions into a nominally heterogeneous process. Active sites may also be lost through hydrolysis, neutralisation, poisoning or chemical transformation without necessarily being released into the reaction medium. Consequently, declining activity should not be attributed to leaching alone unless elemental analysis, hot filtration testing or analysis of the liquid phase provides supporting evidence.

- **Structural and thermal degradation:** Biochars produced at relatively low pyrolysis temperatures generally possess less condensed carbon frameworks and may be more susceptible to changes in pore structure, surface chemistry and mechanical integrity during repeated reaction and regeneration. Exposure to heat, reactive media or oxidative regeneration can collapse or enlarge pores, remove surface functionalities, oxidise the carbon framework or cause catalyst attrition. These changes may reduce active-site accessibility even when the active species remain chemically present.
- **Sintering and active-phase agglomeration:** In metal or metal-oxide functionalised biochar catalysts, prolonged thermal exposure or repeated high-temperature regeneration may promote particle migration, crystallite growth and agglomeration. The resulting reduction in active-phase dispersion and exposed surface area decreases the number of accessible catalytic sites. Weak metal-support interactions and non-uniform active-phase distribution may further increase susceptibility to sintering.

The fundamental deactivation mechanisms affecting biochar-based catalysts are not entirely distinct from those observed for conventional heterogeneous supports; coking, pore blockage, leaching and sintering can also occur in silica- and zeolite-supported systems. However, the heterogeneous carbon framework of biochar influences the extent and reversibility of these processes. Depending on the feedstock and preparation conditions, biochar may contain interconnected macro- and mesopores that improve the transport of bulky triglycerides and FFAs. Such broader pore-size distributions may delay complete pore blockage in some biochars, although this advantage has not been demonstrated consistently across catalyst systems. Surface defects and oxygen-containing functionalities can also provide anchoring sites for incorporated catalytic species. Nevertheless, these potential advantages depend strongly on feedstock selection and preparation conditions. Irregular pore connectivity, variable mineral content and non-uniform surface chemistry can produce uneven active-site distributions and inconsistent deactivation behaviour. Furthermore, acidic or basic functionalities may be lost through hydrolysis or leaching, while insufficiently anchored metal species may migrate or agglomerate during repeated operation [127–129].

In comparison, ordered mesoporous silicas such as SBA-15 and MCM-41 provide more uniform pore dimensions, reproducible surface chemistry and controlled active-phase dispersion, whereas zeolites possess crystalline frameworks with well-defined acidity and generally high thermal stability. These characteristics permit more reproducible control of active-site location and make structural changes during regeneration easier to interpret. However, zeolite micropores may restrict the diffusion of triglycerides and are susceptible to rapid activity loss when coke or heavy organic species block their narrow channels. Ordered mesoporous silicas provide better accessibility for bulky reactants, but supported or grafted active species may still leach if their interaction with the silica surface is insufficiently strong. Biochar, therefore, cannot be regarded as inherently more resistant to deactivation than either support. Its broader pore-size distribution may provide an advantage in accommodating bulky reactants and deposits, but its chemically heterogeneous framework complicates active-site retention and reproducibility. Biochar also presents a specific regeneration limitation: oxidative treatments used to burn off coke from thermally stable silica or zeolite supports may simultaneously oxidise the carbon framework and remove carbon-bound functional groups. Consequently, regeneration of biochar-based catalysts generally requires more carefully controlled temperature and atmosphere than regeneration of inorganic supports [130–133].

The extent to which these degradation mechanisms influence catalytic performance depends on the nature of the biochar support, the embedded active species, and the operating conditions used during biodiesel synthesis. While catalyst deactivation is often unavoidable during prolonged use, many of these effects can be mitigated or reversed through appropriate regeneration processes. Accordingly, understanding the relationship between deactivation behaviour and recovery is essential for extending catalyst lifespan and improving the long-term sustainability of biochar-based catalytic systems.

4.2. Regeneration strategies

Regeneration is central to extending the operational lifespan of biochar-based catalysts, particularly when catalyst deactivation arises from predominantly reversible processes such as coke deposition, adsorbed reaction intermediates, or weakly bound impurities [134]. In biodiesel production, effective recovery should restore catalytic activity without significantly altering the carbon framework, removing active functional groups, or causing further loss of incorporated metal or basic species. Therefore, recovery strategies must be evaluated not only by the extent of activity recovery, but also by their effect on catalyst structure, chemical durability, and long-term reuse potential.

Several regeneration approaches have been investigated to restore the activity of spent biochar-based catalysts, with their effectiveness largely dependent on the dominant deactivation mechanism. Thermal regeneration can effectively remove carbonaceous deposits; however, regeneration conditions must be carefully controlled to minimise oxidation of the biochar support. Appropriate temperature, atmosphere, and treatment duration should be selected according to the catalyst composition and regeneration objective to preserve structural integrity and active-site functionality. Chemical re-functionalisation using acidic or alkaline reagents can successfully replenish depleted active centres, although it increases reagent consumption, processing complexity, and operational costs. In contrast, solvent washing with methanol or ethanol offers a simple, low-cost approach for removing weakly adsorbed reactants and by-products. Still, it is generally ineffective against strongly bound coke deposits or irreversible structural degradation. Hybrid regeneration methods that combine thermal and chemical treatments have attracted growing attention, as they offer a more balanced approach to restoring catalytic activity while preserving the structural integrity of biochar catalysts [135–139].

Direct laboratory-scale regeneration studies on biochar-based biodiesel catalysts remain considerably less common than conventional reuse tests. As previously noted, Ribeiro et al**.** reported an initial ester content of 97.20% using sodium-functionalised murici-seed biochar. Beyond the five reuse cycles discussed in Section 2.5.2, the spent catalyst was regenerated through sodium-silicate re-impregnation followed by thermal treatment at 400 °C under N_2. The ester content recovered to 96.71% in the first post-regeneration cycle and remained at 95.93 and 94.96% during the next two cycles, before declining to 75.32% by the tenth overall cycle. This behaviour shows that replenishing the sodium-containing active phase restored activity temporarily, although it did not prevent subsequent deactivation [97]. Wang et al. similarly reported that a calcium-loaded municipal-sludge biochar catalyst retained a biodiesel yield of 84.9% after ten alternating catalysis and regeneration cycles. The authors attributed the superior stability to the porous biochar matrix and naturally occurring SiO_2 [140]. These studies demonstrate the potential of regeneration to extend catalyst utilisation, but differences in catalyst composition, recovery procedures and performance metrics currently prevent direct comparison of regeneration efficiency.

The selection of a regeneration method, therefore, involves a trade-off between activity recovery, processing cost and preservation of the

catalyst structure. Solvent washing is operationally simple and requires relatively mild conditions, making it appropriate when deactivation is caused predominantly by adsorbed oil, glycerol or reaction intermediates. However, solvent purchase, recovery and disposal increase material and environmental burdens, and washing cannot restore active species lost through leaching. Thermal regeneration can remove strongly retained organic deposits more effectively, but its energy demand and requirement for controlled atmospheres increase operating costs; excessive temperature may also oxidise the carbon framework, remove oxygen-containing or sulfonic functional groups, and promote sintering of supported particles. Chemical re-functionalisation can replenish leached acidic or basic species and may provide greater activity recovery, but it effectively introduces an additional catalyst-preparation stage involving reagents, washing, drying and waste generation. Hybrid thermal–chemical treatments may deliver more complete activity restoration, although their additional energy and chemical requirements must be justified by a sufficiently large extension of catalyst lifetime. Consequently, the most economically favourable strategy is not necessarily the method giving the highest single-cycle activity recovery, but the treatment that provides the lowest cumulative cost and environmental burden per unit of biodiesel produced over the catalyst lifetime. However, published studies rarely report regeneration energy consumption, solvent recovery, catalyst mass loss or treatment costs. Consequently, the present cost–benefit comparison remains qualitative, and direct economic comparisons among regeneration methods are not yet possible [141–143].

Systematic investigations of regeneration protocols for biochar-based biodiesel catalysts remain limited, as most studies evaluate catalyst reuse rather than activity restoration following confirmed deactivation [144–146]. Future studies should identify the dominant deactivation mechanism, quantify activity recovery and catalyst mass loss, and characterise the spent and regenerated materials. Regeneration studies should also report the energy, reagent, solvent and waste requirements of the treatment. These data are needed to compare regeneration efficiency and establish whether repeated recovery improves the economic and environmental performance of biodiesel production. Pilot- and industrial-scale regeneration evidence also remains extremely limited, as most available results originate from short laboratory-scale batch experiments.

4.3. Reusability and stability assessment

Reusability and regeneration should be distinguished when assessing catalyst longevity. Reusability describes the recovery and repeated application of a catalyst, typically after separation, washing and drying, whereas regeneration involves an additional treatment intended to restore activity that has already been lost. A catalyst that retains a high FAME yield after several reuse cycles may demonstrate operational durability, but this observation alone does not establish active-site retention or structural stability. Apparent performance may also be influenced by catalyst loss during recovery, leached species remaining in the reaction medium, or variations in the quantity of catalyst returned to each cycle. Reuse studies should therefore report the catalyst-recovery procedure, recovered dry mass, activity during every cycle and whether fresh catalyst or active species were added between runs [147–149].

A robust stability assessment should combine cycle-resolved catalytic performance with leaching measurements, hot-filtration or filtrate-activity tests, and characterisation of the fresh, spent and regenerated catalysts. Techniques such as ICP-OES or ICP-MS can quantify leached metal species, while elemental analysis or XPS can monitor the retention of sulfur- or nitrogen-containing functionalities. BET analysis, XRD, FTIR, Raman spectroscopy, electron microscopy and acid- or base-site measurements can reveal pore blockage, structural degradation, particle agglomeration and changes in active-site density [150,151]. For industrial evaluation, the number of reuse cycles should be considered together with cumulative biodiesel production per unit mass of catalyst, regeneration frequency, catalyst make-up requirements, product contamination and the energy and material inputs associated with recovery. Continuous or semicontinuous testing under realistic feedstock conditions is ultimately required because short batch-reuse experiments cannot fully represent catalyst attrition, fouling and long-term performance at a process scale.

4.4. Industrial considerations and future perspectives

Despite the encouraging catalytic performance demonstrated at laboratory scale, the successful industrial implementation of biochar-based catalysts requires consistent catalytic activity, prolonged operational stability, and cost-effective regeneration over extended periods of use. In addition to maintaining catalyst activity, large-scale application will depend on the availability of reproducible biochar materials with consistent physicochemical properties, reliable regeneration protocols, and predictable performance across different biodiesel feedstocks [152,153]. Overcoming these practical considerations is essential to ensuring that the advantages demonstrated under laboratory conditions translate into economically viable and sustainable industrial processes.

Although numerous studies have demonstrated the promising catalytic performance of biochar-based catalysts under laboratory conditions, translating these findings to industrial biodiesel synthesis remains a significant challenge [154–156]. Variations in biomass feedstocks, biochar production methods, catalyst functionalisation, and reaction conditions often result in inconsistent catalyst properties and performance, limiting reproducibility across studies. The absence of standardised testing protocols makes direct comparisons between catalysts difficult and complicates identifying the most promising systems for large-scale implementation. Addressing these challenges will require greater emphasis on pilot-scale validation, standardised evaluation methodologies, and integrated techno-economic and life-cycle assessments to establish the practical feasibility of biochar-based catalysts under realistic operating conditions.

5. Comparative analysis of biochar and conventional support materials

Catalyst support selection for biodiesel production cannot be based on catalytic activity alone. Practical implementation also depends on the support's textural and surface characteristics, long-term durability, regeneration potential, production requirements, and environmental implications. A meaningful comparison between biochar and conventional support materials must consider not only reaction performance, but also the economic and operational factors that determine whether a catalyst can be prepared reproducibly, recovered, and reused at larger scales.

Conventional catalyst supports, including zeolites, mesoporous silicas, metal oxides, alumina, and activated carbon, have been widely employed in FAME production because they offer a range of surface areas, well-defined pore structures, and favourable thermal and mechanical stability. However, these materials often require energy-intensive synthesis, non-renewable precursors, or extensive post-synthesis modification, increasing both production costs and environmental impacts. These limitations have motivated the search for more sustainable catalyst support materials [157,158].

Fig. 10 summarises the principal advantages and limitations of the major catalyst support materials used in biodiesel production [159,160]. Although biochar has emerged as a promising catalyst support, comparatively few studies have systematically evaluated its performance against conventional support materials under comparable conditions. This limitation is particularly evident in the South African context, where the catalytic potential of locally derived biochars under industrially relevant conditions remains largely unexplored. Addressing this knowledge gap is essential to translating abundant biomass

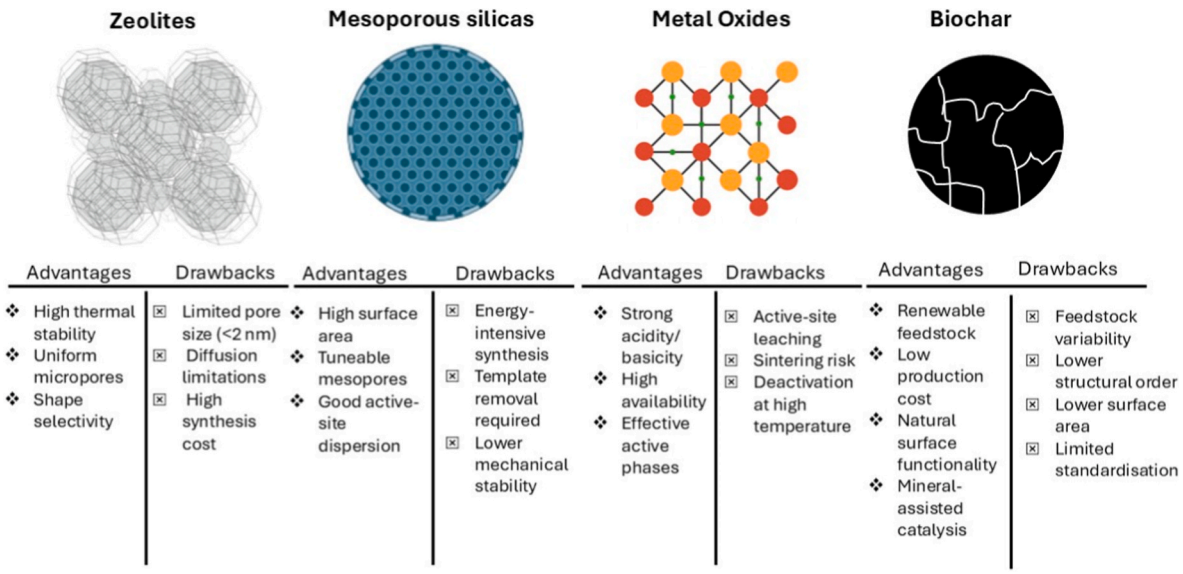


Fig. 10. Comparative assessment of the key advantages and limitations of conventional catalyst supports and biochar for biodiesel production.

resources into practical, economically viable catalyst technologies for sustainable biodiesel synthesis.

Although catalyst supports are routinely characterised using XRD, FTIR, Raman spectroscopy, XPS, and EDS, the present comparison focuses on BET surface area analysis, electron microscopy, and temperature-programmed desorption (TPD). These techniques provide complementary information on three features that are particularly relevant to biodiesel catalysis: pore networks, support morphology, and the density and strength of acidic or basic sites. Considered together, these parameters influence reactant transport, active-phase dispersion, and the availability of catalytic centres, providing a practical basis for comparing biochar with conventional support materials.

5.1. *BET surface area and textural properties*

BET surface area analysis provides important information on the surface area, pore volume, and pore-size distribution of catalyst supports, all of which influence reactant diffusion and active-site accessibility during esterification and transesterification. A high surface area increases the area available for active-phase dispersion and exposes a greater proportion of existing catalytic centres; however, pore architecture is equally important in biodiesel synthesis. In particular, mesopores are advantageous because they facilitate the diffusion of bulky triglyceride molecules, whereas excessive microporosity may restrict mass transfer and limit access to active centres.

Mesoporous silicas, particularly SBA-15, typically exhibit exceptionally high BET surface areas (600 - 900 m^2/g) and uniform mesopores of approximately 6 -10 nm, providing excellent accessibility to catalytically active sites and efficient reactant diffusion [161]. By comparison, biochars generally possess lower BET surface areas (200-600 m^2/g), although these values vary considerably depending on biomass feedstock, pyrolysis conditions, and activation strategy. Biochar frequently exhibits a hierarchical pore network comprising micropores, mesopores, and macropores, which can improve mass transport and catalyst wetting during biodiesel synthesis. Therefore, although engineered supports often achieve higher absolute surface areas, biochar's broader pore framework may compensate for these differences by enhancing reactant availability under practical reaction conditions [162].

Comparative studies have demonstrated that BET surface area is strongly influenced by biomass feedstock and preparation conditions, highlighting that textural properties are not intrinsic to the support material itself but depend on its production. In a comparative study by Saidi et al. (2023), biochar synthesised from rice husk and pyrolysed at 700 °C exhibited a specific surface area of 177 m^2/g, reflecting its moderately porous structure [163]. In contrast, Narowska et al. (2020) investigated activated carbon derived from beech tree wood, which demonstrated a significantly lower surface area of 72 m^2/g. This disparity highlights how biomass type and processing conditions can greatly influence the textural characteristics of carbonaceous supports [164]. These findings demonstrate that differences in BET surface area cannot be interpreted independently of feedstock selection and synthesis methodology. Direct comparisons between catalyst supports based solely on BET values should be approached with caution, as pore connectivity and surface chemistry also govern the accessibility and effectiveness of catalytic sites.

Although chemically activated carbons and synthetic mesoporous supports frequently exhibit higher BET surface areas than biochar, surface area alone is not a reliable predictor of catalytic performance in biodiesel production. The availability of active centres, hierarchical pore architecture, surface composition, and mass-transfer characteristics collectively influence catalytic efficiency more than BET surface area alone. Appropriately engineered biochars have achieved reported biodiesel yields within the same broad range as several conventional supported catalysts, although direct performance equivalence has not been established. Such materials may also offer advantages associated with renewable precursors and potentially simpler preparation routes.

5.2. *Morphological characteristics of catalyst supports*

Catalyst morphology plays an important role in determining the dispersion of active species, pore connectivity, and mass transport during biodiesel synthesis. While ordered supports such as mesoporous silicas provide uniform pore channels and controlled particle architecture, biochar-derived supports often exhibit heterogeneous and hierarchical morphologies inherited from their biomass precursors [165]. SEM and TEM analyses provide useful insight into how structural order, pore connectivity, and surface roughness influence catalyst-support performance beyond surface area alone.

Representative SEM micrographs of biochar, activated carbon, and SBA-15 are presented in Fig. 11 [166–168]. Although all three materials possess porous structures suitable for catalyst-support applications, their morphologies differ considerably. Biochar typically retains the heterogeneous cellular architecture of its biomass precursor, resulting in an interconnected hierarchical pore network. Activated carbon generally

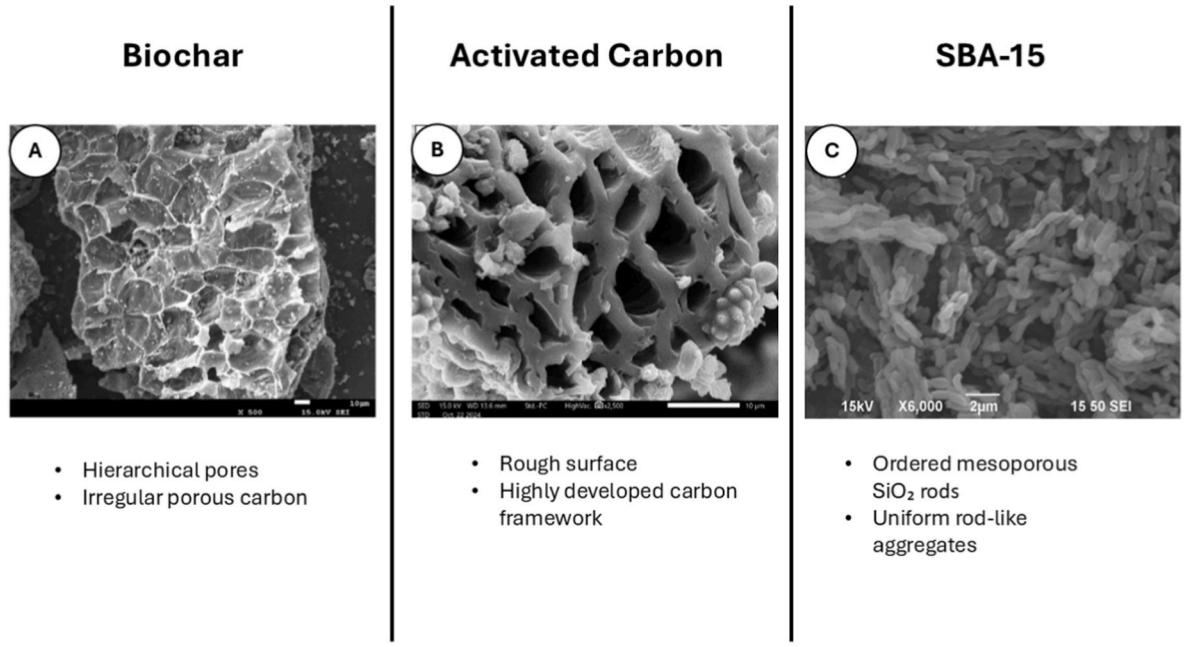


Fig. 11. Representative SEM micrographs comparing the morphology of biochar, activated carbon, and SBA-15 catalyst supports. Images are reproduced from representative studies, and the original scale bars have been retained. Reproduced with permission from Ref. [166] (Copyright © 2018 Elsevier), Ref. [167] (Copyright © 2026 Elsevier), and Ref. [168] (Copyright © 2014 Elsevier).

exhibits a rough, highly developed porous carbon framework following chemical activation, whereas SBA-15 possesses a highly ordered mesoporous silica structure composed of uniform rod-like particles. These contrasting morphologies illustrate the structural diversity of catalyst supports employed for biodiesel production and provide a visual basis for comparing their influence on catalyst performance.

Comparative SEM and TEM studies demonstrate that the principal distinction between biochar and conventional catalyst supports lies in the degree of structural order rather than the presence of porosity itself. Biochar commonly exhibits heterogeneous and hierarchical pore frameworks containing macro-, meso-, and micropores, as observed for spent malt rootlet-derived biochar by Vakros et al. [169] and biomass-derived honeycomb-like structures reported by Suman et al. [170]. In contrast, mesoporous silicas such as SBA-15 typically form relatively uniform rod-like particle aggregates and contain an ordered hexagonal mesopore network with uniform mesopore channels of approximately 9 nm, thereby supporting effective catalyst anchoring through their highly ordered mesoporous architecture [171]. Nevertheless, recent TEM investigations by Yu et al. [172] showed that shrimp shell-derived hierarchical biochar also exhibits interconnected pore networks that support effective catalyst anchoring and reactant transport despite its less-ordered morphology.

These studies demonstrate that morphological uniformity alone is not sufficient to predict catalyst performance in biodiesel production. Although conventional supports such as mesoporous silicas provide highly ordered pores that facilitate precise control over active-site dispersion, other supports, including activated carbon and biochar, derive their catalytic behaviour from more heterogeneous surface structures. Catalyst morphology should be evaluated in conjunction with pore architecture, surface chemistry, and active-site accessibility rather than structural order alone. Among carbonaceous supports, activated carbon can provide comparable surface roughness and accessible pore networks but typically requires chemical activation using agents such as KOH or $ZnCl_2$ to achieve these characteristics, often at the expense of carbon yield and with additional environmental considerations [173]. In contrast, biochar can retain a functional hierarchical morphology through comparatively simple pyrolysis routes, offering a favourable balance between structural integrity and catalytic functionality.

The literature indicates that the catalytic significance of morphology lies not in the degree of structural order, but in the functional organisation and connectivity of the pore network.

5.3. TPD analysis of acid-base sites

The density, strength, and distribution of acidic and basic sites are among the most influential physicochemical attributes governing catalyst performance in biodiesel production. Acidic sites promote esterification by protonating free fatty acids (FFAs), whereas basic sites facilitate transesterification by generating methoxide ions from short-chain alcohols. Thus, catalyst supports possessing appropriately balanced acid-base characteristics are particularly attractive for processing low-quality feedstocks containing both triglycerides and high concentrations of FFAs. Temperature-programmed desorption (TPD) provides valuable insight into these surface properties by quantifying the density and strength of acidic and basic sites [174–176].

Unlike conventional catalyst supports, the acidic and basic properties of biochar can be tailored through careful selection of biomass feedstock, pyrolysis conditions, and post-synthesis modification. The density and distribution of surface acid-base sites vary considerably among biochars, enabling their catalytic behaviour to be tuned for esterification, transesterification, or bifunctional catalysis. The wide range of acidity and basicity values reported in Table 6 illustrates this variability, showing that biochar does not have a single, fixed surface composition but rather a tunable physicochemical character that depends strongly on its preparation method.

Direct numerical comparison of the acid- and base-site densities reported in Table 6 is not appropriate because the values were obtained in separate studies using different experimental protocols. Reported TPD results depend on the probe molecule, sample pretreatment, adsorbate exposure, purge conditions, heating rate, final desorption temperature, carrier-gas flow rate, peak-deconvolution or integration method, and whether site density is normalised to catalyst mass or surface area. Differences in the temperature ranges used to classify weak, medium and strong sites further complicate comparisons of acid or base strength. Consequently, the values in Table 6 should be interpreted only as

Table 6
Representative acid- and base-site densities reported for differently prepared biochars using NH_3-TPD and CO_2-TPD, respectively [177–180]. Values originate from separate studies and are not directly comparable because the analytical protocols differ.

Study (year)	Feedstock & treatment	Acidity (mmol/g, NH_3-TPD)	Basicity (mmol/g, CO_2-TPD)
Adilina et al. (2021)	Oil-palm empty fruit bunch, untreated	0.15	0.50
Dehkhoda et al. (2013)	Rice husk, KOH activation	0.70	-
Ringsby et al. (2024)	Pine sawdust/sewage sludge, KOH activation	-	2.35
Zaparoli et al. (2023)	açaí seed, untreated	-	5.14

representative examples of the tunability of biochar surface chemistry and not as a quantitative ranking of the listed catalysts. Reliable numerical comparison would require the materials to be analysed using the same instrument, pretreatment procedure, desorption programme and data-processing method.

Biochar may contain intrinsic acidic or basic surface groups derived from oxygen-containing functional groups, heteroatoms, and residual minerals, while pyrolysis and post-synthesis modification provide additional control over its density and strength. Activated carbon generally requires chemical oxidation or acid/base treatment to introduce comparable surface functionalities, whereas mesoporous silicas and metal oxides exhibit material-specific acid-base properties; CaO and MgO are strongly basic, alumina contains predominantly Lewis-acidic sites, and oxides such as TiO_2 may display amphoteric behaviour [181]. The principal distinction between biochar and conventional supports lies not only in the density of acidic and basic sites, but also in the origin and tunability of these active functional groups. For bifunctional systems, the relative strength and spatial separation of acidic and basic centres are also important, since poorly controlled proximity may reduce effective site density or promote undesirable interactions.

Although a high density of acidic or basic sites is generally associated with improved catalytic activity, site density alone does not determine catalyst performance. Equally important are the strength, accessibility, distribution, and balance of these active sites, which collectively govern reaction pathways and catalytic selectivity during FAME production [182]. In this respect, biochar offers a distinct advantage because its surface composition can be tailored to provide predominantly acidic, predominantly basic, or bifunctional catalytic behaviour through appropriate feedstock selection and modification strategies. This tunability may allow biochar-based catalysts to be designed for feedstocks with different FFA content, while supporting both esterification and transesterification within a single catalytic system.

The wide variation in acid–base site densities reported in the literature indicates that catalyst supports cannot be ranked solely by TPD values. Instead, these measurements provide insight into a material's surface chemistry and should be interpreted alongside its textural and morphological characteristics when evaluating catalytic behaviour.

5.4. Comparative catalytic performance and structure-performance interpretation

A quantitative comparison of reported catalytic performance is provided in Table 7. The selected studies represent biochar, activated carbon, ordered mesoporous silica, zeolite and metal-oxide support systems. However, the data were generated using different feedstocks, catalyst compositions, reaction temperatures, alcohol-to-oil ratios, catalyst loadings and performance metrics. The table, therefore, provides a structured comparison of the operating requirements and reported outcomes rather than a direct ranking of support materials. A statistically valid assessment of the independent influence of the support would require the same active phase to be deposited at comparable loading on each support and tested using an identical feedstock, reactor configuration and analytical method.

Table 7 shows that high biodiesel yields have been reported for all five support classes, but these values were achieved under substantially different operating conditions. Das et al.'s bifunctional biochar and Olagunju et al.'s activated-carbon-supported CaO systems both achieved yields above 96% under comparatively moderate reaction times, although the catalysts, feedstocks and reactor configurations differed. Lazdovica et al.'s CaO–MgO/SBA-15 catalyst achieved a biodiesel yield of 97.8 wt% at 95 °C over 4 h, whereas Yusuf et al.'s β-zeolite-supported catalyst required 200 °C and 8 h to obtain 96.9% conversion [183–187]. Although both systems produced high reported values, their different feedstocks, active phases and reaction conditions prevent a direct assessment of the independent effect of the support. Their reported performance, therefore, cannot be attributed solely to the ordered structures or surface areas of the supports. Conversely, the lower surface area or less-ordered morphology of a biochar does not necessarily indicate inferior catalytic performance when accessible acid or base sites and suitable transport pathways are present.

The comparison also illustrates why BET surface area cannot be isolated as a universal predictor of biodiesel yield. Catalytic performance reflects the combined effects of active-phase identity and loading, acid- or base-site density and strength, pore accessibility, feedstock composition, temperature and mass-transfer conditions. Because these variables were not standardised across the selected studies, the available literature does not demonstrate that biochar universally matches or outperforms activated carbon, silica, zeolite or metal-oxide supports. Instead, it indicates that appropriately functionalised biochar can reach a similar range of reported yields while potentially using renewable precursors and less structurally uniform pore networks. Confirming a genuine support effect will require controlled studies in which the same

Table 7
Selected performance data for biochar-based catalysts and catalysts supported on activated carbon, mesoporous silica, zeolite and metal oxides. Values originate from independent studies conducted under different conditions and should not be interpreted as a direct performance ranking.

Study and support class	Catalyst system	Feedstock	Reaction conditions	Reported performance	Reusability or regeneration	Reference
Das et al. (2026) - Biochar	Sulfonated nitrogen-doped bifunctional biochar	Used vegetable oil	82.3 °C, 25.1 min; methanol-to-oil ratio 19.2:1; 5 wt.% catalyst	98% biodiesel yield	Biodiesel yield remained above 90% in the sixth cycle.	[183]
Olagunju et al. (2022) -Activated Carbon	CaO supported on activated carbon	Soybean oil	65 °C; 90 min; methanol-to-oil ratio 4.2:1; 3.0 wt.% catalyst	96.9% biodiesel yield	Not reported	[184]
Lazdovica et al. (2024) — Mesoporous Silica	0.3-CaO–MgO/SBA-15	Rapeseed oil	95 °C; 4 h; methanol-to-oil ratio 15:1; 5 wt.% catalyst	97.8 % biodiesel yield	Not reported	[185]
Yusuf et al. (2023) - Zeolite	SO_4^{2-}/ZnO–β-zeolite	Waste cooking oil	200 °C; 8 h; methanol-to-oil ratio 15:1; 3.0 wt.% catalyst	96.9% conversion	Retained 80.89% of its initial activity after the third cycle	[186]
Yusuff and Owolabi (2019) - Metal-Oxide Support	Alumina-supported coconut-chaff catalyst	Waste frying oil	65 °C; 2.5 h; methanol-to-oil ratio 12:1; 1.5 wt.% catalyst	91.05% biodiesel yield	Biodiesel yield declined from 90.15 to 75.57 wt.% after five cycles	[187]

active phase is deposited at comparable loading on different supports and tested under identical reaction and reuse conditions.

Reusability evidence is similarly inconsistent. Das et al.'s bifunctional biochar catalyst maintained a biodiesel yield above 90% in the sixth cycle, whereas Yusuf et al.'s zeolite-supported catalyst retained 80.89% of its initial activity after the third cycle and while quantitative reuse data were not reported for Lazdovica et al.'s CaO–MgO/SBA-15 system. Yusuff and Owolabi reported a decline from 90.15 to 75.57 wt.% biodiesel yield after five cycles [183,184,186,187]. These outcomes represent different forms of durability and cannot be compared directly without consistent information on recovered catalyst mass, leaching, regeneration inputs and spent-catalyst properties. Future comparative studies should therefore report cycle-resolved yield, catalyst recovery, active-species retention and regeneration requirements alongside conventional textural and catalytic measurements.

Downstream process compatibility provides an additional basis for comparing catalyst supports. Regardless of the support material, crude biodiesel may contain residual methanol, glycerol, unreacted glycerides, FFAs, soaps, water, fine catalyst particles and leached active species. Solid catalysts can simplify processing when they are retained by filtration, centrifugation or within a fixed-bed reactor; however, the practical benefit depends on particle size, mechanical strength, settling behaviour and resistance to leaching rather than support composition alone. Finely divided biochar and activated carbon may require centrifugation or fine filtration to prevent carbon-particle carryover, while attrition of silica, zeolite or metal-oxide particles can create similar solid-removal requirements. Leaching of K-, Na- or Ca-containing phases is particularly important because residual inorganic species may contaminate the biodiesel and require additional washing or adsorption steps. Therefore, a high catalytic yield does not necessarily correspond to a simpler downstream process if catalyst recovery is incomplete or active species enter the liquid product [188,189].

The adsorption properties of the support may also influence purification. Fadhil et al. demonstrated that activated carbon prepared from spent tea waste removed impurities from crude biodiesel and provided higher product yields and improved fuel properties relative to silica gel and conventional water washing [190]. Similarly, Catarino et al. showed that fumed silica removed residual oil, glycerol, calcium soaps and leached calcium from biodiesel produced using a Ca-based heterogeneous catalyst [191]. These findings demonstrate the potential of carbonaceous and silica materials as dry-washing adsorbents, although their performance as separate purification media should not automatically be attributed to the same materials when used as catalyst supports. Strong adsorption may assist impurity removal, although the adsorption behaviour of a separate purification medium cannot be assumed to represent that of the same material when used as a catalyst support. Consequently, support selection should consider catalyst recovery, solid carryover, active-species leaching, glycerol separation, methanol recovery and the need for wet or dry polishing before the biodiesel can comply with ASTM D6751 or EN 14214 [192,193].

6. Potential and perspectives of biochar-based catalysts in South Africa

Although biochar-based catalysts possess many of the physicochemical and catalytic attributes required for biodiesel production, strong laboratory performance does not necessarily translate into commercial viability. Practical implementation depends on scientific, technical, economic, logistical, and regulatory factors that extend beyond catalyst design alone. South Africa provides a relevant case study because of its substantial lignocellulosic resource base, developing bioeconomy, and need for lower-carbon fuel technologies [194]. This section evaluates the opportunities and constraints of implementing biochar-based catalysts in South Africa and identifies considerations applicable to other biomass-rich regions.

6.1. South African biomass resources and feedstock potential

South Africa has a diverse, well-established lignocellulosic biomass resource base that provides a strong foundation for the sustainable production of biochar-based catalyst supports. Large quantities of agricultural residues, forestry by-products, agro-industrial wastes, and invasive alien plant species are generated annually, representing a potentially valuable source of carbon-rich feedstocks for biochar production [195]. Their conversion into catalytic materials offers a route for linking residue management with value-added biodiesel technologies. Resource availability alone, however, does not establish industrial feasibility, because the useable fraction depends on collection, competing applications, feedstock consistency, and regional logistics.

The value of South Africa's biomass resource base lies not only in the quantities generated but also in the diversity and regional distribution of the available residues. Table 8 summarises representative agricultural and forestry streams, their estimated annual availability, principal producing provinces, and current uses [196–199]. These values provide a more evidence-based indication of feedstock potential; however, gross residue generation should not be interpreted as the quantity immediately available for catalyst manufacture. Practical supply will also depend on collection efficiency, seasonal availability, transport distance, competing uses, moisture content, and the consistency of the resulting biochar.

The values in Table 8 indicate that no single residue stream needs to carry the full burden of future catalyst production. Sugarcane bagasse and maize stover offer substantial agricultural resources, while forestry residues provide an additional supply distributed across major timber-producing regions. Wheat straw is available in smaller quantities and is subject to competing agricultural uses, which may limit the recoverable fraction. A diversified supply model could improve resilience by allowing catalyst producers to select residues according to regional availability, transport requirements, competing demand, and the biochar properties required for a specific catalytic application.

Quantitative feedstock assessment must also consider the lipid substrates available for biodiesel production. South Africa produced approximately 2.80 Mt of soybeans and 0.70 Mt of sunflower seed in 2025, indicating a substantial domestic oilseed-processing base [200]. These figures represent total crop production rather than quantities available exclusively for biodiesel, because food, feed and edible oil markets account for substantial competing demand. Waste cooking oil, therefore, represents a strategically important non-food alternative. Although a consolidated national inventory of recoverable waste cooking oil is not presently available. The South African Women in Biodiesel project proposed the establishment of ten decentralised women-owned enterprises, with a combined target of producing at least three million litres of biodiesel annually from used cooking oil collected from restaurants, fast-food outlets and supermarkets [201]. Earlier surveys of South African used-oil biodiesel facilities reported production capacities ranging from approximately 100 to 8000 L day^{-1}, illustrating both the availability of this feedstock and the predominantly small and decentralised scale of its conversion [202]. These quantities should therefore be interpreted as indicators of technical and logistical potential rather than estimates of the entire nationally recoverable resource.

Despite this favourable resource base, translating biomass into a reliable source of biochar catalysts remains challenging. Agricultural residues are often geographically dispersed, seasonally generated, and subject to competing uses such as animal feed, soil amendment, combustion, or bioenergy production. Variations in moisture content, ash chemistry, and biomass composition can also affect the reproducibility of biochar properties, reinforcing the need for standardised feedstock selection and processing protocols. These considerations suggest that a principal barrier to industrial implementation in South Africa is not gross biomass availability alone, but the establishment of reliable systems for residue collection, feedstock standardisation and conversion into reproducible catalyst materials [203,204].

Table 8
Estimated annual availability, regional distribution, and current utilisation of major South African lignocellulosic residues with potential for biochar production.

Biomass Residue	Estimated total residue generated (South Africa)	Major producing provinces	Current utilisation	Biochar Potential	Reason	Reference
Sugarcane bagasse	7.6 Mt yr^{-1}	KwaZulu-Natal, Mpumalanga	Cogeneration, disposal, bioenergy	High	Large annual production, concentrated generation at sugar mills, established collection infrastructure.	[196]
Maize stover	5.15 Mt yr^{-1}	Free State, Mpumalanga, Northern Cape	Livestock fodder, soil retention, bioenergy	High	High residue production and widespread availability, although seasonal.	[197]
Forestry residues	3.5 Mt yr^{-1}	KwaZulu-Natal, Mpumalanga, Eastern Cape	Wood pellets, cogeneration, livestock fodder, bioenergy	High	Continuous generation from the forestry and timber industries with substantial resource volumes.	[198]
Wheat straw	0.6 – 1.0 Mt yr^{-1}	Northern Cape, Free State, Western Cape	Livestock bedding, disposal, bioenergy	Moderate	Lower annual production and significant competing agricultural uses (animal bedding, livestock feed, soil retention).	[199]

6.2. Biochar catalysts from local feedstocks: what works and What's missing

Among the biomass feedstocks investigated for biodiesel catalysis, sugarcane bagasse has emerged as one of the most promising precursors for producing biochar-based catalysts. This is particularly relevant to South Africa, where sugarcane processing generates substantial quantities of bagasse annually, providing an abundant and readily available lignocellulosic residue for value-added applications. International studies have demonstrated that sulfonated and chemically activated sugarcane bagasse-derived biochars can achieve FAME conversions of up to 98–99% under optimised reaction conditions, highlighting the potential of this agricultural residue as an effective catalyst support for biodiesel production [205–207].

South African researchers have made substantial progress in producing and characterising biochars from locally relevant biomass resources for applications including soil amendment, contaminant adsorption, wastewater treatment and electrochemical energy systems [208,209]. Related advances have also been reported in biomass-derived heterogeneous catalysts for biodiesel production. For example, Maseko et al. prepared a silica xerogel from sugarcane leaves collected in South Africa and obtained a biodiesel yield of 96.9% from canola oil under optimised conditions. However, this material consisted principally of biogenic silica rather than biochar and therefore does not provide direct experimental validation of a locally sourced biochar catalyst support [210].

A targeted examination of the literature identified by this review found very limited published experimental evidence in which a South African biomass residue was converted into biochar, functionalised or loaded with an active phase, and subsequently evaluated as a heterogeneous catalyst or catalyst support for biodiesel synthesis. Mojapelo et al. recently examined the potential of waste-derived biochar matrices as supports for biomagnetic bifunctional catalysts for the conversion of spent oils, demonstrating growing South African interest in this research direction [211]. Nevertheless, the limited number of locally validated catalyst systems, rather than an assumed absence of all related research, remains the central evidence gap. Relevant studies may also exist as theses, conference contributions or ongoing projects that are not represented in the peer-reviewed literature. Accordingly, systematic experimental studies using clearly identified South African biomass and lipid feedstocks are still required before the technical feasibility of a domestic biochar-supported biodiesel-catalyst value chain can be established.

Advancing biochar-based catalysts beyond laboratory-scale demonstrations will require a more comprehensive research framework that integrates feedstock selection, biochar synthesis, catalyst functionalisation, physicochemical characterisation, and catalytic performance into a single, cohesive approach. Equally important is incorporating catalyst regeneration, process optimisation, and techno-economic evaluation to determine the practical viability of these systems. Establishing such a framework would strengthen the reproducibility and scalability of biochar catalyst research while providing a foundation for pilot-scale validation and eventual industrial implementation, both in South Africa and in other biomass-rich regions.

6.3. Policy context and industrial relevance in South Africa

South Africa has established a policy environment that increasingly favours renewable fuels, greenhouse gas mitigation, and the utilisation of biomass within a circular bioeconomy. National initiatives, including the South African Biofuels Regulatory Framework (2020), the Carbon Tax Act (No. 15 of 2019), and broader renewable energy strategies, provide incentives for technologies that reduce dependence on fossil-derived fuels and promote lower-carbon production [212,213]. Although these policies do not explicitly address biochar-based catalysts, they create a favourable legislative environment for sustainable biodiesel production and the valorisation of biomass residues.

Despite this supportive policy landscape, legislative incentives alone are unlikely to drive industrial adoption of biochar-based catalysts. Commercial deployment depends on demonstrating that these materials can consistently satisfy technical, economic, and operational requirements under realistic production conditions. While laboratory studies have established the catalytic potential of biochar [214–216], considerably less attention has been given to questions of manufacturing consistency, catalyst lifetime, regeneration, process integration, and compatibility with existing biodiesel-processing infrastructure. These considerations determine whether a promising laboratory catalyst can become a commercially viable technology.

The importance of integrating techno-economic assessment (TEA) and life-cycle assessment (LCA) into biomass-based energy research has already been recognised within the South African context. Previous studies evaluating biorefineries, biofuel production systems, and biomass utilisation have shown that commercial implementation depends not only on technical performance, but also on production costs, feedstock logistics, greenhouse gas emissions, resource efficiency, and overall process sustainability. These integrated assessments provide a more comprehensive understanding of whether laboratory-scale technologies remain economically viable and environmentally beneficial when translated to industrial production. However, comparable evaluations specifically addressing biochar-based catalysts for biodiesel production remain largely unavailable, representing an important barrier to commercial implementation [217–220].

A meaningful life-cycle assessment of biochar-based biodiesel catalysts should extend beyond the origin of the biomass and account for the energy and material requirements of the complete catalyst–fuel system. The assessment boundary should include biomass collection and transport; feedstock drying and size reduction; pyrolysis and inert-gas consumption; physical or chemical activation; acid, base or metal

functionalisation; catalyst washing and neutralisation; biodiesel reaction heating; methanol recovery; product separation; catalyst regeneration; and final catalyst management. Particular attention should be given to electricity and thermal-energy consumption because high-temperature pyrolysis, activation and repeated regeneration may offset part of the environmental benefit associated with using a waste-derived carbon support. Water consumption, acidic or alkaline wastewater, spent activation reagents, solvent emissions, glycerol-containing streams and catalyst losses should likewise be included rather than treating the biochar catalyst as an environmentally burden-free input [221–223].

Waste-derived biochar may provide life-cycle benefits by diverting residues from uncontrolled burning or disposal, reducing demand for virgin support materials and retaining a fraction of biomass-derived carbon within a comparatively stable solid matrix. These benefits are nevertheless conditional on the residue's alternative use, the source of process energy, transport requirements, biochar yield, chemical consumption, catalyst lifetime and end-of-life pathway. Hosseinzadeh-Bandbafha et al., for example, found that the transesterification and purification stages were major contributors to the environmental burden of waste-cooking-oil biodiesel produced using a sulfonated magnetic biochar catalyst, demonstrating that use of waste-derived feedstocks does not remove the need to optimise reaction and downstream-processing inputs [224]. This caution is particularly relevant in South Africa, where Stephenson et al. reported that the greenhouse-gas performance of biodiesel varied substantially with crop yield, irrigation and land-use assumptions: favourable scenarios produced lower impacts than fossil diesel, whereas cultivation requiring irrigation and conversion of previously uncultivated land could result in higher impacts [225]. Future South African assessments should therefore compare biochar-supported catalysts with conventional catalyst systems using a common functional unit, consistent system boundaries and alternative scenarios for electricity supply, feedstock allocation, catalyst reuse, regeneration and end-of-life carbon management.

From an industrial perspective, demonstrating catalytic activity alone is insufficient to justify commercial adoption. Biochar-based catalysts must also be evaluated for economic feasibility, environmental performance, process scalability, and long-term operational reliability. Addressing these requirements will require robust techno-economic assessments, life-cycle analyses, pilot-scale demonstrations, and collaboration among academia, industry, and policy stakeholders to determine whether laboratory-scale catalyst performance can translate into commercially viable biodiesel conversion. The significance of biochar-based catalysts, however, extends beyond catalytic performance alone. By converting underutilised biomass residues into functional catalyst materials that support renewable FAME production, biochar offers an opportunity to address waste valorisation and renewable energy generation simultaneously. These broader environmental and socio-economic benefits reinforce the potential contribution of biochar catalysts to circular bioeconomy strategies and provide stronger scientific and commercial justification for their continued development and industrial deployment.

6.4. *Strategic research roadmap for advancing biochar-based catalysts in South Africa*

Four interrelated research gaps currently limit the translation of biochar-based biodiesel catalysts into practical applications in South Africa. First, although abundant lignocellulosic feedstocks such as sugarcane bagasse, maize stover and forestry residues are available, very few published South African studies have experimentally evaluated locally derived biochars as catalyst supports for biodiesel production. Secondly, techno-economic analyses, life-cycle assessments, and carbon accounting studies evaluating the feasibility of locally produced biochar catalysts remain scarce, making it difficult to assess their commercial competitiveness and environmental benefits. Thirdly, integrated assessments linking catalyst reuse, carbon retention, end-of-life management, and biodiesel production remain limited, despite the potential to generate multiple environmental and economic benefits from a single biomass resource. Finally, the development of multifunctional biochar catalysts, particularly hybrid systems containing both acidic and basic active sites tailored to locally relevant feedstocks such as waste cooking oil, remains largely unexplored. To address these interconnected research gaps and resource priorities, this paper proposes a strategic framework to guide the future development of biochar-based catalysts for sustainable biodiesel synthesis in South Africa, as illustrated in Fig. 12.

These resource and logistical considerations indicate that research should not assign equal priority to every possible biomass–lipid combination. The first priority should be acid-functionalised or bifunctional biochar produced from sugarcane bagasse and evaluated with waste cooking oil. Bagasse is generated in large, concentrated quantities at established sugar-processing facilities, particularly in KwaZulu-Natal and Mpumalanga, thereby offering more favourable collection and preprocessing conditions than geographically dispersed agricultural residues [196]. Waste cooking oil is a non-food lipid feedstock with an existing, although decentralised, South African collection and biodiesel-production base. Because its free-fatty-acid and water contents can vary substantially, it also provides an appropriate test substrate for determining whether bifunctional biochar catalysts can combine esterification and transesterification under practically relevant conditions. Maize-stover-derived biochar should be investigated subsequently because of its high national availability, but its seasonal and geographically dispersed supply, together with its competing uses as livestock feed and for soil protection, may increase collection costs and reduce the sustainably recoverable fraction [197]. A second priority should pair forestry-residue-derived biochar with waste cooking oil in KwaZulu-Natal, Mpumalanga and the Eastern Cape, where forestry residues are generated comparatively continuously and could support regional catalyst-production systems [198]. Refined sunflower and soybean oils may be retained as standardised laboratory substrates for catalyst benchmarking, but their competing food and feed uses make them less appropriate than waste oils as the primary feedstocks for an initial South African deployment strategy.

To translate the three strategic pillars into an operational research programme, the proposed framework should be implemented through short-, medium- and long-term stages with measurable decision points. Table 9 presents provisional stage-gate indicators for determining whether a locally derived catalyst should progress from laboratory screening to pilot-scale validation and eventual industrial demonstration. These indicators are proposed research targets rather than universally established commercial thresholds and should be refined

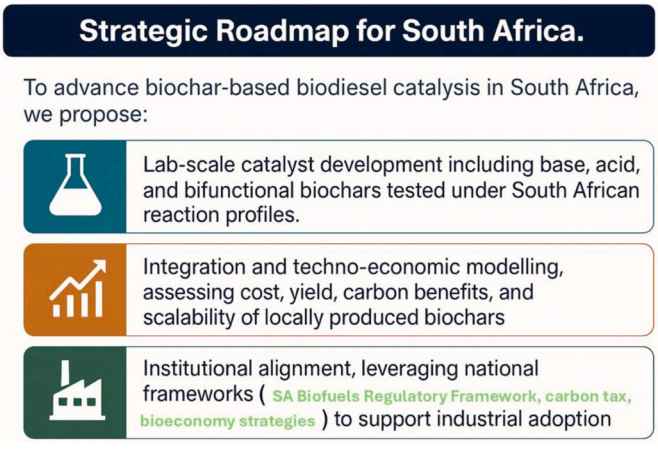


Fig. 12. Proposed strategic roadmap for advancing biochar-based catalyst development for sustainable biodiesel production in South Africa.

Table 9
Proposed research priorities and validation criteria for advancing South African biochar-based biodiesel catalysts [226–229].

Research period	Scientific priorities	Proposed validation criteria
Short term (0–2 years)	Laboratory screening of prioritised South African biomass–lipid combinations	Initial FAME yield ≥90% as a screening target; biodiesel ester content meeting the applicable fuel standard; reproducibility across independently prepared catalysts; at least five reuse cycles; active-phase leaching measured using ICP-OES or ICP-MS rather than inferred solely from retained yield.
Medium term (3–5 years)	Scale-up of catalyst preparation and testing with compositionally variable waste cooking oil	At least ten reaction–regeneration cycles; batch-to-batch catalyst reproducibility; hot-filtration testing; characterisation of fresh and spent catalysts; extended batch-sequence or continuous testing to determine the deactivation rate rather than assuming stability from a small number of reuse cycles.
Long term (>5 years)	Pilot-scale validation and process integration	Demonstrated catalyst lifetime under continuous or repeated operation; consistent product quality under variable feedstock conditions; leached metals remaining within the limits of the selected biodiesel standard; quantified energy consumption, greenhouse-gas emissions, waste generation and catalyst-replacement requirements.

through techno-economic assessment, life-cycle assessment and consultation with South African biodiesel producers.

The proposed indicators are intended as research-stage decision criteria rather than universal industrial specifications. The ≥90% initial FAME yield represents a screening target informed by the performance range of high-yielding biochar catalysts reviewed in this paper, whereas compliance should ultimately be determined from the complete fuel-quality requirements of the applicable biodiesel standard. Five reuse cycles provide evidence of preliminary recyclability, but longer testing, leaching measurements and spent-catalyst characterisation are required before catalyst durability can be established.

The proposed framework is structured around three complementary pillars that collectively provide a coordinated pathway for advancing biochar-based catalysts from laboratory research to industrial applications. Rather than representing independent research priorities, these pillars should be viewed as interconnected components of a unified development strategy. The first pillar emphasises laboratory-scale catalyst development using locally available biomass feedstocks, including optimising acidic, basic, and bifunctional biochars under reaction conditions relevant to South African biodiesel production. Building this experimental foundation is essential for establishing catalyst performance, stability, regeneration behaviour, and compatibility with locally available feedstocks and waste cooking oils.

The second pillar extends beyond catalyst generation by incorporating techno-economic modelling, life-cycle assessment, and process integration to determine whether promising laboratory catalysts remain economically and environmentally competitive at larger production scales. Evaluating catalyst cost, FAME yield, carbon benefits, and scalability alongside catalytic performance enables more realistic assessments of commercial viability while directly addressing the practical considerations required for industrial adoption.

The final pillar recognises that successful commercial deployment depends not only on scientific and engineering advances but also on alignment with the broader policy and industrial landscape. Integrating catalyst development with national initiatives such as the Biofuels Regulatory Framework, the Carbon Tax Act, and broader bioeconomy and renewable energy strategies provides opportunities to support sustainable industrial growth while promoting biomass valorisation and lower-carbon fuel production. Together, these three pillars establish a coordinated pathway that integrates catalyst development, engineering evaluation, and policy alignment into a single strategy for advancing biochar-based catalysts beyond laboratory research. While developed to address the specific opportunities and challenges of South Africa's biodiesel sector, the pathway offers a transferable approach that may also guide the sustainable advancement of biochar catalyst technologies in other biomass-rich regions.

Overall, the near-term opportunity for South Africa lies in establishing experimentally validated catalyst–feedstock combinations based on locally concentrated biomass residues and non-food lipid resources. Sugarcane-bagasse- and forestry-residue-derived biochars evaluated with waste cooking oil represent logical starting points, but their practical value must be demonstrated through reproducible catalyst preparation, direct leaching measurements, regeneration studies and testing under compositionally variable feedstock conditions. Subsequent progress should move beyond isolated yield optimisation towards extended catalyst operation, fuel-quality verification, process integration and comparative life-cycle and techno-economic assessment. This staged approach would provide the evidence required to determine whether biochar-based catalysts offer measurable technical and environmental advantages over conventional supports within the South African biodiesel sector.

7. Conclusion

The available literature demonstrates the potential of biochar as both a heterogeneous catalyst and a tunable catalyst support for biodiesel production, rather than merely as a low-cost carbonaceous material. Depending on its composition and modification, catalytic activity may originate from native minerals, grafted acidic or basic functional groups, or active phases dispersed across the carbon framework. Its pore network, surface composition, acid–base behaviour, and capacity to anchor active species can be tailored through feedstock selection, thermochemical conversion, activation, functionalisation, and active-phase incorporation. Catalytic performance cannot be attributed to a single parameter, such as BET surface area or active-site density, but rather arises from interactions among pore connectivity, reactant accessibility, surface functionality, active-phase dispersion, active-site stability, and resistance to deactivation. These structure–performance relationships are central to the rational design of acidic, basic, and bifunctional biochar-based catalysts for esterification, transesterification, and the conversion of low-quality lipid feedstocks. Biochar also offers advantages that extend beyond initial catalytic activity. Its production from agricultural, forestry, and agro-industrial residues links heterogeneous catalyst development with waste valorisation and reduces reliance on support materials derived from non-renewable or highly processed precursors. Compared with activated carbon, mesoporous silica, zeolites, and metal oxides, biochar generally provides less structural uniformity but greater flexibility in feedstock selection, surface modification, and acid–base functionalisation. These benefits do not make biochar universally superior; rather, they position it as a complementary catalyst platform whose suitability depends on balancing catalytic activity, active-site retention, structural durability, separation behaviour, regeneration potential, downstream process compatibility, preparation requirements, and process economics. Moreover, differences in catalyst preparation, lipid feedstocks, reaction conditions, and analytical methods currently prevent reliable numerical ranking across unrelated studies and limit the establishment of universal structure–performance thresholds.

The principal challenge is no longer demonstrating that biochar-

based catalysts can achieve high biodiesel yields but establishing whether their performance can be reproduced and sustained under practical operating conditions. Future research should integrate feedstock standardisation, reproducible catalyst synthesis, standardised catalytic testing, post-reaction characterisation, active-site leaching assessment, regeneration, pilot-scale validation, techno-economic assessment, and life-cycle analysis within a single development strategy. Progression from laboratory development to industrial application should be guided by measurable performance targets for biodiesel yield, catalyst lifetime, active-site leaching, regeneration, and process sustainability. In South Africa, collaboration among research institutions, biomass-producing industries, biodiesel processors, and policymakers will be essential for converting the country's substantial residue streams into reliable catalyst materials. Addressing these priorities could position biochar-based catalysts as a practical component of more circular and potentially lower-carbon biodiesel production in South Africa, while providing a transferable approach for other biomass-rich regions seeking to combine renewable fuel development with circular resource utilisation.

CRediT authorship contribution statement

Tatum Matthews: Writing – original draft, Methodology, Investigation, Formal analysis, Conceptualization. **Ntalane Sello Seroka:** Writing – review & editing, Validation, Supervision, Methodology, Conceptualization. **Lindiwe Khotseng:** Writing – review & editing, Resources, Project administration, Funding acquisition, Conceptualization.

Data availability

Data used is available in the article.

Funding

This research was funded by the National Research Foundation: RCHDI24121926979 and BRIC231102160232.

Conflicts of interest

The authors declare no conflicts of interest.

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