International Journal of Energy
ISSN: 2957-9473 | Vol. 9, No. 2, 2026

Research Progress on Fe-Loaded Biochar for Promoting the Co-Combustion of Coke Breeze

Yuchen Li, Lili Li, Bo Wang

School of Materials and Metallurgical Engineering, University of Science and Technology Liaoning, Anshan, Liaoning, China

Abstract: Coke breeze remains an indispensable solid fuel in iron ore sintering and several high-temperature metallurgical combustion systems, but its high ignition temperature, poor burnout, and coupled CO/NOx emissions constrain clean and low-carbon utilization. Biochar derived from biomass is a promising partial substitute because of its renewable carbon origin, developed pore structure, and relatively high intrinsic reactivity. However, the rapid combustion of biochar, the large difference in mineral composition relative to coke breeze, and instability under harsh thermal conditions often limit its direct use. Fe loading provides a practical route to integrate fuel substitution with catalytic promotion. Recent studies on coal/biochar co-combustion, coke combustion catalysis, Fe-loaded char catalysts, and iron ore sintering indicate that Fe-loaded biochar can improve oxygen transfer, construct Fe-O-C interfacial active sites, accelerate the oxidation and gasification of carbon, and promote heterogeneous NO reduction while suppressing incomplete combustion. This review summarizes recent progress in feedstock selection, preparation methods, structure-property relationships, combustion and kinetic behavior, interfacial mechanisms, ash transformation, deactivation, and engineering prospects of Fe-loaded biochar for coke-breeze co-combustion. Particular attention is paid to the synergy among Fe redox cycles, alkali/alkaline-earth metals, and defect-rich carbon matrices. Finally, major knowledge gaps are identified, including the lack of in situ evidence under realistic heating rates, scale bridging from thermogravimetric tests to packed beds, and long-term stability evaluation in real metallurgical atmospheres.

Keywords: Fe Loading; Biochar; Coke Breeze; Co-combustion; Catalytic Combustion; Iron Ore Sintering; NOx Control.

1. Introduction

The decarbonization of iron and steel production has intensified research on renewable carbon carriers capable of partially replacing fossil-derived coke and coal. Among different metallurgical fuel streams, coke breeze is of particular importance because it supplies heat to the sintering bed, controls the flame-front profile, and affects the mineralization of the final sinter. Nevertheless, coke breeze has a relatively high ignition temperature and limited intrinsic reactivity, and under unfavorable local atmospheres it can generate high levels of CO and NOx. Biochar has therefore attracted attention as an alternative carbon source because it is produced from renewable biomass and usually exhibits higher porosity, more defective carbon structures, and higher reactivity than coke or anthracite [1-5].

In iron ore sintering and related high-temperature combustion systems, however, direct substitution of coke breeze by raw biomass or even untreated biochar is not straightforward. Raw biomass carries excessive volatiles and moisture, whereas biochar may combust too quickly, disturb bed permeability, or alter ash melting behavior because of its higher contents of K, Na, Ca, Mg, Si, and P. A growing body of work shows that the performance of biomass-derived char depends strongly on feedstock type, pyrolysis severity, particle size, and mineral composition [3,5-8]. These observations suggest that a “drop-in” replacement strategy is unlikely to be optimal; instead, the carbon matrix of biochar should be rationally engineered for the target metallurgical environment.

Fe loading is emerging as one of the most promising modification routes. In the broader carbon conversion literature, Fe species supported on char or biochar have been widely studied for tar reforming, gasification, steam reforming, methane decomposition, and heterogeneous NO reduction [9-16]. In parallel, Fe-containing catalysts and iron-rich raw materials have been shown to accelerate coke combustion and influence CO/NO emissions during sintering [17-21]. These two streams of research converge toward the concept that Fe-loaded biochar can act simultaneously as a renewable fuel, a catalytic carrier, and an interfacial promoter for coke-breeze co-combustion.

Despite the rapid increase in related publications, there is still no dedicated review focusing on Fe-loaded biochar as a promoter for the co-combustion of coke breeze. Existing reviews usually address biochar utilization in iron and steel production, coal/biomass co-conversion, or iron-based catalytic thermochemical conversion separately [4,5,12,22-24]. The present review aims to fill this gap by critically discussing preparation strategies, physicochemical characteristics, combustion performance, kinetic features, mechanistic understanding, ash-related risks, and engineering prospects. The scope includes iron ore sintering as the primary application scenario, while insights from fluidized beds, blast-furnace raceways, and char-catalyzed reduction systems are incorporated when they help explain general principles.

2. Preparation and Physicochemical Characteristics of Fe-loaded Biochar

The first determinant of performance is the biomass precursor. Wood residues, sawdust, corn stover, rice husk, coconut shell, sunflower husk, and other agricultural residues have all been used to prepare biochar for metallurgical applications [5-8,25]. Feedstocks richer in lignin usually produce chars with higher fixed-carbon content and better mechanical strength, whereas herbaceous biomass often contributes more alkali and alkaline-earth metals (AAEM), which can either promote conversion or aggravate low-temperature ash melting. From the perspective of coke-breeze co-combustion, the desirable precursor should generate a char with moderate reactivity, stable particle morphology, low sulfur and chlorine, and a mineral profile that does not excessively deteriorate sinter quality.

Pyrolysis conditions also strongly regulate char structure. Slow pyrolysis between 500 and 800 °C generally increases fixed carbon and decreases volatile matter, while more severe treatment tends to reduce surface oxygen groups and collapse fragile pore walls. Several studies on metallurgical biochar have shown that chars produced at around 700-800 °C can provide a useful compromise between carbon enrichment and structural integrity [5,7,26]. For Fe-loaded systems, an additional concern is the interaction between Fe precursors and biomass oxygen functionalities during heating. Co-pyrolysis with iron salts may anchor Fe species more uniformly, whereas post-pyrolysis impregnation offers better control over loading amount and phase evolution.

Common Fe sources include $Fe(NO_3)_3$, $FeCl_3$, $FeSO_4$, ferric citrate, hematite, magnetite, mill scale, and Fe-rich industrial residues [10,13,18,27]. Impregnation remains the most widely used route because it is simple and can distribute Fe species into the pore network of biochar. Precipitation, hydrothermal deposition, and mechanochemical mixing have also been reported. In practical terms, Fe loading should be high enough to create abundant catalytic sites but not so high that Fe oxide particles block pores, reduce accessible surface area, or cause severe ash fusion problems. The optimum level varies with the precursor and process, but many studies suggest that moderate loading provides the best balance between activity and structural preservation [10,13,28].

Characterization of Fe-loaded biochar typically combines proximate/ultimate analysis with BET surface area, SEM-EDS, XRD, Raman spectroscopy, XPS, temperature-programmed desorption/reduction, and thermogravimetry coupled with FTIR or MS [9-14,28]. A recurring conclusion is that Fe loading can increase defect density, create oxygen-transfer sites, and alter the graphitization degree of the carbon matrix. Equally important is the formation of Fe-O-C interfacial structures, which differ fundamentally from a mere physical mixture of oxide particles and inert carbon. Such interfaces are often invoked to explain the enhanced activation of O_2, CO_2, H_2O, and NO over Fe-loaded carbon materials [11,14-16].

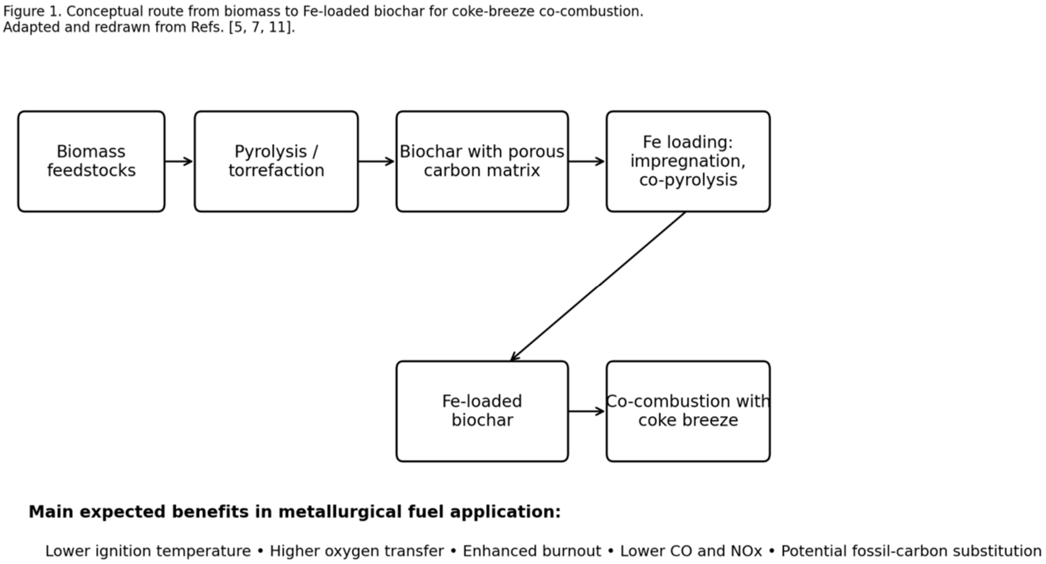

Figure 1. Conceptual route from biomass to Fe-loaded biochar for coke-breeze co-combustion. Adapted and redrawn from Refs. [5, 7, 11]

3. Combustion Behavior of Fe-loaded Biochar/Coke-breeze Blends

The most direct benefit of adding biochar to coke breeze is usually a reduction in ignition temperature and a shorter burnout time. This trend is consistent with the higher porosity and greater defect density of biochar relative to coke breeze [2,3,29]. When Fe is additionally introduced, ignition can be further facilitated because Fe oxides promote oxygen adsorption-dissociation and accelerate the formation of active surface oxygen complexes. Thermogravimetric studies on biochar/coal or char/coke blends commonly show earlier mass-loss onset and higher maximum combustion rates than predicted by linear addition, indicating positive synergy under suitable blending ratios [2,29-32].

In iron ore sintering, combustion behavior is governed not only by single-particle reactivity but also by the distribution of heat release in granules and across the bed. Zhou et al. reported that the combustion behavior of coke and biomass char in granules strongly depends on their physicochemical properties and distribution states [3]. Other sintering studies demonstrated that replacing a portion of coke breeze with charcoal or biochar can maintain or even improve sinter quality when the substitution level is appropriately controlled [6-8,25]. These observations imply that Fe-loaded biochar is most promising as a partial rather than total replacement fuel, where its high reactivity can compensate for the sluggish combustion of coke breeze without destabilizing the thermal front.

The gas atmosphere also matters. In air, Fe-loaded biochar mainly improves oxygen transfer and the oxidation of carbonaceous intermediates, thus decreasing residual char and CO formation. In CO_2- or H_2O-containing atmospheres, additional benefits arise from catalyzed gasification and from the redox cycling of Fe species. Such coupling is relevant to the lower-oxygen microenvironments that frequently develop inside sintering granules or near the flame front. Under these conditions, the gasification of carbon by CO_2 or H_2O can interact with oxidation and modify local CO/CO_2 ratios, which in turn affects NO reduction pathways [17,18,21,33].

Blend ratio, particle size, and contact mode are equally important. Too little Fe-loaded biochar may not generate enough catalytic interfaces, whereas too much may lead to premature heat release, reduced bed permeability, and undesirable ash chemistry. Closer particle-size matching and intimate mixing generally favor synergy because the heat and gas released from the biochar particle can interact more effectively with adjacent coke-breeze particles. By contrast, segregation tends to reduce the co-combustion advantage and may create localized hot or cold zones. The optimal design therefore depends on both intrinsic reactivity and mesoscale fuel distribution [3,6,8,20].

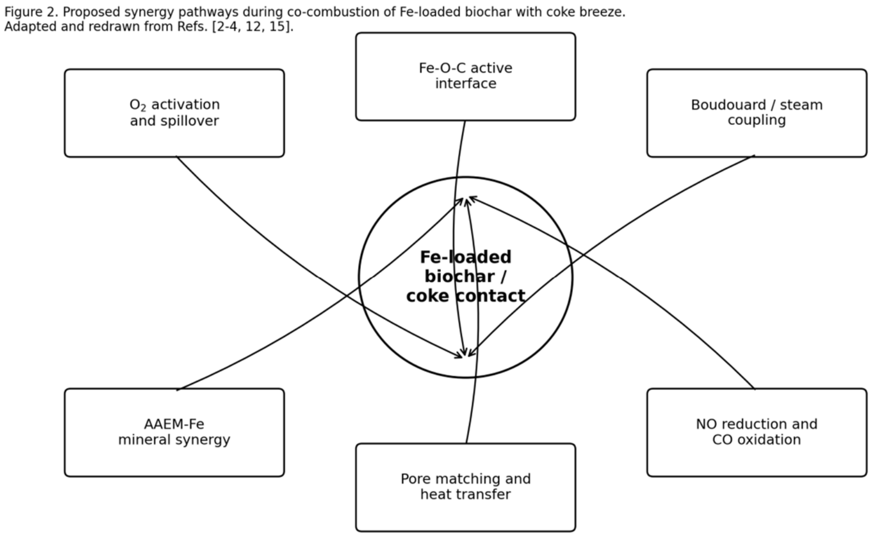

Figure 2. Proposed synergy pathways during co-combustion of Fe-loaded biochar with coke breeze. Adapted and redrawn from Refs. [2-4, 12, 15]

4. Kinetic Features and Origin of Synergy

Most laboratory studies assess apparent kinetics using thermogravimetric methods such as Flynn-Wall-Ozawa, Kissinger-Akahira-Sunose, Starink, or Coats-Redfern analyses. Across the literature, biochar usually exhibits lower apparent activation energy than coke breeze or coal char because its carbon skeleton contains more defects and its pores facilitate oxidant diffusion [2,29,31,34]. When positive synergy occurs in mixed fuels, the experimental conversion curve deviates from the weighted sum of the individual fuels, and the apparent activation energy decreases accordingly. Fe loading usually strengthens this trend by introducing new oxygen-transfer routes and by lowering the energy barrier for carbon oxidation or gasification.

The synergy can be divided into at least three categories. The first is thermal complementarity: highly reactive biochar ignites early and supplies heat that helps coke breeze reach the temperature range where oxidation becomes self-sustaining. The second is interfacial catalysis: Fe-loaded biochar provides active contact points where oxygen-containing species migrate to neighboring carbon sites. The third is mineral synergy: native AAEM species in biomass char may cooperate with Fe to form mixed catalytic centers, which accelerate carbon conversion and alter ash evolution [14,15,35-37]. The relative importance of these contributions depends on the fuel properties and reactor environment.

Kinetic interpretation must nevertheless be treated with caution. Most reported activation energies are "apparent" values derived under low heating rates and small sample sizes, while real sintering beds involve high local temperatures, sharp oxygen gradients, particle-particle shielding, and transient liquid-phase formation. As a result, the activation parameters obtained from thermogravimetry cannot be extrapolated directly to industrial conditions. More realistic reactor-scale studies and multiscale models are needed to couple intrinsic kinetics with granule structure, gas-solid flow, and bed permeability [3,19-21,38].

Table 1. Representative observations reported for biochar/coke or Fe-assisted char systems relevant to coke-breeze co-combustion.

System	Main observation	Implication	Ref.
Biochar replacing coke breeze in sintering	Partial replacement can maintain sinter quality and lower fossil carbon use	Biochar should be used at controlled substitution levels	[6-8,25]
Coke + biomass char in granules	Combustion depends on particle distribution, physicochemical properties, and granule structure	Mesoscale contact is critical to synergy	[3]
Fe-CaO / composite catalysts for coke combustion	Ignition is facilitated and in-situ NO reduction is enhanced	Fe-containing catalysts can tune both heat release and emissions	[17,18]
Fe-loaded char catalysts	Fe-O-C structures and redox cycles accelerate carbon conversion	Fe-loaded biochar is a rational multifunctional promoter	[9-16]
Coal/biochar co-combustion studies	Positive synergy often appears as lower activation energy and faster burnout	Thermal and catalytic complementarity support blend design	[2,29-32]

Another underexplored issue is the kinetic role of Fe phase evolution. During heating, Fe may transform from hydrated salts or amorphous oxides into Fe2O3, Fe3O4, FeO, metallic Fe, or mixed Fe-containing silicates. Each phase differs in oxygen mobility, reducibility, and affinity toward carbon defects. Time-resolved kinetic studies that combine thermogravimetry with in situ XRD, Mössbauer spectroscopy, or X-ray absorption are still rare, yet they are essential for identifying the active Fe state under true co-combustion conditions [11,14,16,39].

5. Mechanistic Understanding

The mechanistic literature converges on the central role of Fe redox cycles. Fe2O3 may be partially reduced by carbon, CO, or H2 to Fe3O4, FeO, or Fe0, and then reoxidized by O2, CO2, or H2O. This cyclic transformation provides a dynamic pathway for oxygen transfer and can accelerate both oxidation and gasification reactions on the carbon surface [11,14,16,39]. In essence, Fe behaves as a shuttle that mobilizes oxygen more efficiently than direct gas-solid contact alone. For coke-breeze co-combustion, this means that the sluggish oxidation of more ordered carbon domains can be assisted by adjacent Fe-loaded biochar particles.

A second key concept is the Fe-O-C interfacial structure. Studies on Fe-supported char catalysts indicate that Fe species interact electronically with edge defects, oxygen functionalities, and aromatic layers of carbon rather than remaining as entirely isolated particles [9-11,14]. These interfaces facilitate the activation of adsorbed oxygen, stabilize reactive carbon-oxygen complexes, and may weaken nearby C-C bonds. The higher defect density of biochar compared with coke breeze is therefore advantageous, because it provides more anchoring sites for Fe species and a larger population of catalytically responsive edge carbons.

The third mechanistic element is the synergy between Fe and native biomass minerals. Potassium, sodium, calcium, and magnesium are well-known promoters of char conversion, although their activity is highly sensitive to speciation and temperature [1,15,35,36]. In Fe-loaded biochar, these components may form mixed oxides, ferrites, or surface complexes that modify oxygen mobility and catalytic stability. Beneficial interactions can accelerate oxidation and NO reduction; adverse interactions can instead promote low-melting mineral phases, encapsulate Fe sites, or increase slagging risk. Distinguishing these effects remains a major challenge, especially when low-cost industrial residues are used as Fe sources.

Emission control constitutes a fourth mechanistic dimension. In high-temperature carbon combustion, NO and CO are often coupled because the local reducing atmosphere created by incomplete combustion can also drive NO reduction. Fe-loaded biochar may lower CO emissions by improving burnout and catalyzing CO oxidation, while its carbon-Fe interface may promote heterogeneous reduction of NO to N2 [15-18,40,41]. This dual action is particularly attractive for sintering, where the control of both heat pattern and gaseous emissions is critical. However, the balance is delicate: if Fe loading or blend design causes severe oxygen deficiency within granules, CO may increase despite the catalytic potential of Fe.

Figure 3. Simplified Fe redox cycle and coupled CO/NO pathways on Fe-loaded carbon surfaces.
Adapted and redrawn from Refs. [16-18, 23].

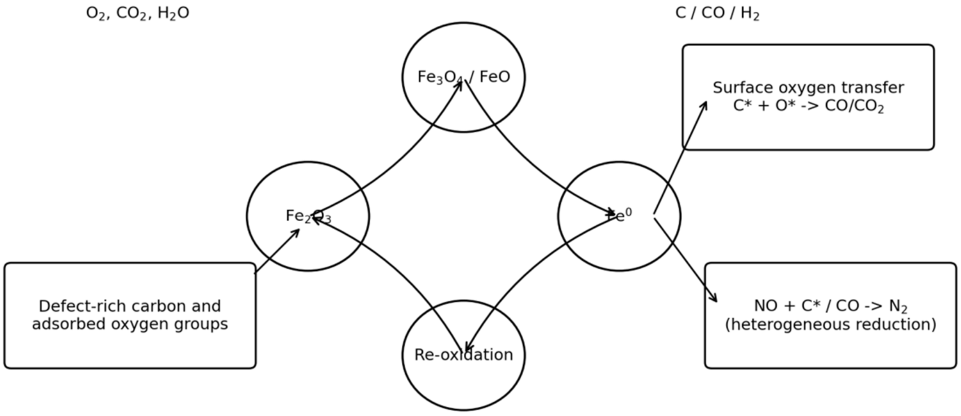

Figure 3. Simplified Fe redox cycle and coupled CO/NO pathways on Fe-loaded carbon surfaces. Adapted and redrawn from Refs. [16-18, 23]

6. Ash Transformation, Deactivation, And Engineering Risks

Ash chemistry is one of the main barriers preventing straightforward industrial adoption. Biochar ash is usually enriched in alkali species and silica, whereas coke-breeze ash often contains more Al, Si, Fe, and Ca from both the fuel and associated mineral matter. When these ashes are mixed and heated, they can produce new eutectics and change liquid-phase generation, viscosity, and mineral assimilation in the sinter bed [6-8,25,42]. Fe loading may intensify these changes because Fe-bearing phases can participate directly in low-melting mineral formation. Therefore, a catalytic benefit at the particle scale does not automatically translate to a bed-scale process advantage.

Deactivation of Fe sites can occur through several routes. High-temperature sintering may cause particle growth and lower dispersion. Silicates and phosphates may encapsulate Fe species. Sulfur and chlorine can poison active sites or change the redox behavior of Fe-containing phases. In addition, repeated thermal shocks may crack fragile chars or detach fine particles from the support [10,13,14,39]. These deactivation routes are familiar in catalysis research but have scarcely been quantified under realistic coke-breeze co-combustion scenarios.

Mechanical and operational issues should also be considered. Many biochars are less dense and more friable than coke breeze, which may alter handling, granulation, and segregation in industrial feed systems. Fe impregnation can either strengthen or weaken the particle, depending on how much salt is introduced and whether it promotes pore collapse during drying and calcination. Moreover, when Fe-rich waste solids such as mill scale or tailings are used as precursors, attention must be paid to trace metals and the consistency of feed composition. The life-cycle benefit of renewable carbon substitution must not be offset by increased dust, problematic ash disposal, or unstable sintering performance [5,11,24,43].

Several studies nevertheless suggest that these risks are manageable when replacement levels are modest and char properties are tailored to the process. Pilot and semi-industrial sintering trials with biochar have reported acceptable productivity and mechanical quality at partial replacement levels, while also showing potential for lower net fossil CO2 emissions [6-8,25]. The challenge for Fe-loaded biochar is to preserve these process-level advantages while introducing additional catalytic functionality. This will require simultaneous optimization of combustion reactivity, ash chemistry, and granule-scale heat release.

7. Engineering Prospects and Future Directions

The most immediate application scenario for Fe-loaded biochar is the partial replacement of coke breeze in iron ore sintering. Here the modified biochar can serve as both a renewable carbon source and an in situ catalyst for combustion and emission control. A second scenario is its use as a functional additive for coke-breeze modification, where only a relatively small mass fraction is introduced to tune ignition and flame-front behavior. A third possibility is co-injection with pulverized coal or auxiliary carbon carriers in the blast-furnace raceway, especially when Fe-containing ash can be incorporated into the burden without adverse effects [20,21,44].

From a research perspective, four priorities stand out. First, the dynamic evolution of Fe phases under realistic heating rates and atmospheres must be resolved with in situ or operando methods. Second, the mesoscale interaction between Fe-loaded biochar and coke-breeze particles must be quantified using combined experiments and models, rather than inferred solely from single-particle thermogravimetry. Third, ash-mineral transformation and deactivation need systematic long-duration testing in pilot beds. Fourth, the techno-economic and life-cycle impacts of different Fe sources should be compared, particularly between analytical-grade salts and low-cost industrial residues [5,11,22,24,43].

Future material design should move from empirical loading toward rational interface engineering. Instead of merely increasing the Fe content, attention should be directed to the spatial distribution of Fe, the creation of stable Fe-O-C motifs, and the coordination with indigenous AAEM species. Hierarchical pores, core-shell deposition, or co-pyrolysis routes may help maintain both accessibility and stability. It is also worthwhile to explore whether mixed Fe-Ca or Fe-Mg systems can deliver higher resistance to ash encapsulation while preserving catalytic activity [17,18,35,37,45].

Ultimately, the success of Fe-loaded biochar will depend on whether it can satisfy three criteria simultaneously: meaningful fossil-carbon substitution, reliable promotion of co-combustion, and compatibility with metallurgical product quality. Meeting all three demands calls for interdisciplinary work linking biomass conversion, catalysis, combustion science, mineral processing, and process metallurgy. The topic is therefore not only scientifically rich but also strategically important for low-carbon ironmaking.

7.1. Advanced Characterization and In-Situ/Operando Diagnostics

A major bottleneck in this field is that the majority of evidence still comes from ex situ characterization before and after combustion, whereas the active structure of Fe-loaded biochar is highly dynamic during heating. Iron nitrate, ferric chloride, steel scale, red mud, and other precursors can all generate different intermediate phases during devolatilization and char oxidation, including Fe2O3, Fe3O4, FeO, metallic Fe, and mixed iron silicates. These phases may transform within seconds as oxygen potential and local gas composition fluctuate around burning particles. Consequently, the apparent catalytic role determined from room-temperature XRD or SEM-EDS images can be only partially representative of the true active state. Future work should therefore adopt in-situ XRD, Raman spectroscopy, diffuse reflectance infrared spectroscopy, high-temperature Mössbauer analysis where available, and environmental TEM on representative samples to capture phase evolution, carbon ordering, and ash encapsulation under realistic atmospheres [8,15,17,23,35,39,45].

For packed beds and sintering-like systems, in-situ optical diagnostics are especially valuable because they connect material evolution with combustion behavior at the particle and bed scales. High-speed imaging, infrared thermography, digital image correlation of bed shrinkage, and online gas analysis can reveal whether Fe-loaded biochar primarily advances ignition, broadens the effective burning zone, or promotes burnout in the tail of the thermal front. Coupling such diagnostics with staged quenching of the bed would make it possible to map the spatial evolution of Fe phases and local mineral assimilation. This kind of spatiotemporal evidence is required to distinguish true catalytic synergy from simple heat-release redistribution caused by the higher reactivity of biochar itself [18-21,33,38,44].

Another underused approach is isotopic or tracer-assisted diagnosis. For example, 18O-labelled oxygen or labelled biomass-derived alkali species could help clarify whether oxygen transfer proceeds mainly through gas-phase activation, lattice oxygen donation from iron oxides, or facilitated spillover across Fe-O-C interfaces. Likewise, selective poisoning experiments and transient pulse tests may separate the contributions of Fe sites, indigenous AAEM species, and defect-rich carbon edges. Such methods have long been used in heterogeneous catalysis, but they remain rare in the literature on coke-breeze substitution and metallurgical co-combustion. Their wider adoption would significantly strengthen mechanistic claims and improve the comparability of results among different precursor systems [23,27,35-37,39].

7.2. Ash Transformation, Alkali Circulation, and Deactivation Pathways

Although catalytic promotion is usually emphasized, the practical lifetime of Fe-loaded biochar depends equally on ash evolution. Biomass-derived chars often contain appreciable amounts of K, Na, Ca, Mg, Si, and P, while coke breeze and sinter feed introduce Fe-bearing minerals, gangue, and fluxes. During co-combustion, these species may interact to form low-melting eutectics, iron silicates, ferrites, aluminates, and phosphate-rich surface layers. Some of these products can be beneficial because they enhance mineral assimilation into the sinter matrix, but others may isolate catalytic iron from the gas-solid interface or alter the permeability of the bed. Hence, ash chemistry is not a secondary issue; it directly determines the persistence, accessibility, and reuse of active Fe sites [6,17,18,22,24,35,42,45,46].

Deactivation can proceed through at least four routes. The first is physical encapsulation of iron nanoparticles or iron oxide clusters by molten ash. The second is chemical incorporation into less reactive phases such as fayalite-like or phosphate-containing compounds. The third is volatilization and redistribution of alkali species, which can initially promote reactivity but later aggravate deposition or induce local sintering of pores. The fourth is carbon-structure collapse in the support itself: rapid burnoff can remove the high-defect matrix that originally stabilized Fe dispersion, leaving larger and less accessible iron-containing residues. Because these routes can occur simultaneously, meaningful deactivation studies should combine thermogravimetry with ash fusion tests, high-temperature microscopy, sequential extraction of metal species, and post-combustion mapping of cross sections from partially reacted particles or packed-bed samples [17,24,35,39,42,46].

Special attention should be paid to cyclic alkali circulation in realistic plants. In industrial sintering, alkalis can evaporate in hot zones and re-condense downstream, creating secondary interactions with newly introduced fuel particles. Fe-loaded biochar may therefore experience a moving chemical environment rather than a fixed one. This means that a formulation appearing stable in single-pass laboratory combustion may behave differently under continuous recycle. Long-duration sinter-pot trials with dust return, or dedicated reactors that emulate alkali condensation and recontact, are urgently needed to evaluate whether Fe-biochar systems remain beneficial after repeated exposure. Without this information, scale-up may overestimate the durability of the material [19,22,24,25,42].

7.3. From Thermogravimetry to Sinter Beds: Scale Bridging and Process Modelling

Thermogravimetric analysis has provided the bulk of kinetic parameters reported for biochar/coke and catalyst-assisted blends, yet TGA conditions differ substantially from industrial operation. Heating rates are usually lower, particle sizes are smaller and more uniform, external mass transfer is simplified, and interactions among neighboring particles, ores, and fluxes are largely absent. As a result, activation energies and synergy indices derived from TGA should be interpreted as comparative descriptors rather than direct design parameters for process optimization. The next stage of research should focus on scale bridging: single-particle tests for intrinsic reactivity, meso-scale packed-bed experiments for coupled heat and mass transfer, and sinter-pot or pilot trials for process response [19,21,29-32,38].

Multiscale modelling can support this transition. At the particle level, shrinking-core or distributed activation-energy frameworks may be expanded to include transient Fe-phase evolution, oxygen spillover, and support consumption. At the bed level, CFD-DEM or continuum porous-media models can track the migration of the flame front, local O2/CO/CO2/NO concentrations, and the thermal interaction between fast-burning Fe-biochar and slow-burning coke-breeze particles. Such models should not merely fit overall burnoff; they should be validated against observable quantities including ignition location, flame-front speed, maximum temperature, bed pressure drop, and spatial gas profiles. Once validated, they can identify operating windows in which Fe-loaded biochar improves both productivity and emission control without sacrificing sinter quality [18-21,33,38,44].

A particularly important modelling issue is whether catalytic promotion and fuel substitution act additively or nonlinearly. If a small amount of Fe-loaded biochar disproportionately accelerates the ignition of adjacent coke breeze, then the optimal dosage may be much lower than would be predicted by a simple replacement calculation. Conversely, if biochar burns too early and leaves insufficient late-stage heat release, the apparent catalyst benefit may vanish at larger substitution ratios. Parametric studies that combine local kinetics with bed-scale heat balance are therefore essential for rational material design. In this sense, the field should move away from reporting only conversion curves and toward integrated performance maps linking material formulation, blend ratio, bed structure, and process outcomes [18,20,21,29,33].

7.4. Techno-economic, Environmental, and Implementation Considerations

For practical deployment, Fe-loaded biochar must be judged not only by reactivity enhancement but also by supply-chain robustness, pretreatment cost, and compatibility with metallurgical operations. Biomass selection influences ash chemistry, carbon yield, grindability, and logistics; Fe precursor selection determines both catalytic performance and economic feasibility. Analytical-grade salts often provide good laboratory reproducibility but may not be realistic at large scale. In contrast, steel scale, pickling sludge, iron-rich ash, red mud, or other low-cost residues could simultaneously reduce material cost and strengthen industrial symbiosis, provided that harmful elements such as chlorine, sulfur, or excessive alkalis are controlled. A complete assessment should therefore compare performance on the basis of both catalytic activity per unit Fe and total system cost per tonne of sinter or per unit CO2 abated [11,22,24,25,43,45].

Life-cycle thinking is equally important. Fe-loaded biochar can generate climate benefits through partial fossil-carbon displacement, potential improvement in combustion efficiency, and the valorization of waste-derived iron sources. However, these benefits can be eroded by energy-intensive drying, impregnation, washing, and multiple heat-treatment steps. The environmental profile further depends on whether biochar production co-generates useful syngas or bio-oil, whether transportation distances are short, and whether the remaining ash is safely assimilated into metallurgical products. Future studies should move beyond qualitative claims and include transparent system boundaries, scenario analysis, and sensitivity studies for biomass moisture, Fe loading level, and substitution ratio [22,24,25,43].

Implementation also requires attention to handling properties. Fine Fe-loaded biochar may differ from coke breeze in density, particle shape, attrition resistance, and moisture uptake, which can influence granulation, bed permeability, and segregation during charging. Therefore, material design should incorporate not only combustion metrics but also powder engineering parameters such as angle of repose, particle-strength distribution, grindability, and interaction with binders or return fines. Such practical constraints often determine whether a promising catalyst-fuel material can be transferred from laboratory studies to stable plant operation [18,19,22,25].

7.5. Recommended Research Roadmap

To accelerate progress, a staged research roadmap is recommended. Stage I should establish reproducible preparation and reporting standards, including biomass source, pyrolysis protocol, Fe precursor chemistry, loading level, washing procedure, and post-treatment atmosphere. Stage II should relate these variables to carbon structure, Fe dispersion, and baseline combustion behavior using a common set of metrics such as ignition temperature, burnout index, apparent activation energy, and normalized NO reduction. Stage III should extend evaluation to meso-scale packed beds and realistic mineral matrices. Stage IV should perform pilot validation and techno-economic/life-cycle analysis. Following such a route would greatly improve comparability among studies and prevent the current fragmentation of data sets [1-5,18,24,29,43].

Table 2. Key research gaps and recommended methods for Fe-loaded biochar/coke-breeze co-combustion.

Research gap	Why it matters	Recommended approach
Transient Fe speciation	Active phases during heating may differ markedly from ex situ products.	Use in-situ XRD/Raman/online gas analysis under sintering-like atmospheres.
Particle-to-bed synergy	TGA cannot capture flame-front redistribution or local oxygen competition.	Combine single-particle tests, packed beds, and sinter-pot validation.
Ash encapsulation and mineral assimilation	Catalytic iron may be either incorporated into useful sinter phases or deactivated.	Perform ash fusion, microprobe mapping, and long-duration exposure tests.
Fe source selection	Low-cost residues may reduce cost but introduce contaminants or variable activity.	Benchmark steel scale, red mud, salts, and iron-rich ashes on a normalized basis.
Scale-up and sustainability	Process gains must offset preparation energy and logistics burden.	Integrate techno-economic assessment with life-cycle and operability metrics.

7.6. Data-driven Screening and Standardized Benchmarking

One reason the literature remains difficult to compare is the absence of standardized benchmarking protocols. Studies differ in biomass type, pyrolysis temperature, Fe precursor, post-washing, particle size, atmosphere, heating rate, and the definition of synergy itself. As a result, even when two reports claim that Fe-loaded biochar improves coke-breeze combustion, the magnitude and mechanism of the effect may not be directly comparable. A useful next step would be to establish benchmark feedstocks and test matrices, for example one woody biomass, one herbaceous biomass, one low-ash coke breeze, and one iron-rich waste precursor, all assessed under a common reporting protocol. Such a database would enable more robust meta-analysis and facilitate the identification of formulation-property-performance relationships [1-5,24,28,29,43].

Data-driven methods can further accelerate material discovery. Once harmonized data sets become available, machine-learning tools could screen the combined influence of ash composition, aromaticity, Fe loading, pore structure, and operating conditions on ignition temperature, burnout index, and NO reduction. Importantly, these models should be used as interpretable aids rather than black boxes. Feature attribution can help reveal whether Fe dispersion, alkali balance, or support porosity dominates under a given atmosphere, thereby guiding rational experiments. In the longer term, open databases and surrogate models may reduce the number of costly pilot trials needed to converge on practical formulations for specific plants or ore blends.

7.7. Industrial Translation: Quality Control, Standards, and Risk Management

Even if the combustion benefits of Fe-loaded biochar are confirmed, industrial translation will depend on quality control and risk management. Biomass feedstocks vary seasonally and geographically, and low-cost iron-bearing residues can show large fluctuations in particle size, contaminant levels, and oxidation state. Therefore, procurement specifications must be developed for moisture, ash chemistry, chlorine, sulfur, trace metals, and Fe availability. Routine acceptance tests should also include at least one rapid combustion indicator and one handling-property indicator. Without such control, plant trials may produce inconsistent results that obscure the intrinsic merits of the concept and undermine operator confidence.

Risk management should additionally consider downstream product quality. In sintering applications, the key question is not simply whether the fuel burns faster, but whether its ash and catalytic residues are assimilated without harming tumble strength, reducibility, or reduction degradation index. The acceptable operating window may thus depend on the ore blend and flux regime of each facility. Pilot demonstrations should therefore report both combustion/emission data and sinter-quality indices, with mass-balance tracking of iron and major ash-forming elements. This integrated reporting style would make future studies substantially more valuable for industrial decision-making [18,19,22,25,45].

Finally, the safest pathway to implementation may be progressive substitution rather than direct high-ratio replacement. Small additions of Fe-loaded biochar as a functional ignition promoter or NO-control additive could be tested first, followed by moderate co-combustion ratios once bed thermal behavior and product quality are verified. This staged strategy is consistent with industrial practice, where operability and reliability often outweigh maximum theoretical carbon substitution. It also aligns with the broader conclusion of this review: Fe-loaded biochar should be developed not merely as a renewable fuel, but as an engineered multifunctional material tailored to the realities of metallurgical combustion systems.

Table 3. Suggested benchmarking metrics for laboratory-to-pilot evaluation.

Evaluation level	Typical outputs	Minimum recommended metrics
Material characterization	Carbon structure and Fe state	Surface area, Raman ID/IG, XRD Fe phases, ash chemistry, Fe loading efficiency
TGA/small reactor	Intrinsic reactivity	Ignition temperature, Tmax, burnout index, apparent activation energy, gas evolution
Single particle/packed bed	Local interaction	Flame-front speed, local temperature profile, O2/CO/CO2/NO distribution
Sinter-pot/pilot	Process response	Productivity, fuel rate, emissions, bed pressure drop, dust behavior
Product assessment	Metallurgical compatibility	Sinter strength/reducibility indices and ash/mineral mass balance

8. Conclusion

Fe-loaded biochar represents a promising multifunctional material for promoting the co-combustion of coke breeze in iron ore sintering and related metallurgical systems. Compared with untreated biochar, Fe-loaded biochar can provide stronger oxygen-transfer capability, more active interfacial sites, faster ignition, and improved burnout. Compared with using Fe catalysts alone, the biochar matrix offers renewable carbon, high defect density, and intimate contact with reacting carbonaceous particles. Existing literature strongly suggests that the performance enhancement originates from the coupling of Fe redox cycles, Fe-O-C interfacial activation, and AAEM-assisted mineral catalysis. At the same time, process-level limitations - especially ash melting, Fe-site deactivation, and scale-up uncertainty - remain significant. Future progress will depend on operando characterization, multiscale modeling, and pilot-scale validation. With these advances, Fe-loaded biochar may become an effective route for combining low-carbon substitution with catalytic intensification in metallurgical combustion.

References

[1] Nzihou A, Stanmore B, Sharrock P. A review of catalysts for the gasification of biomass char, with some reference to coal. Energy, 2013, 58: 305-317.

[2] Zhu G, Wen C, Liu T, et al. Combustion and co-combustion of biochar: combustion performance and pollutant emissions. Applied Energy, 2024, 376: 124292.

[3] Zhou M, Zhao J, Zhang L, et al. Investigation on the combustion behaviors of coke and biomass char based on its physicochemical characteristics and distribution states in iron ore granules. Journal of the Energy Institute, 2020, 93: 1737-1748.

[4] Tchapda A H, Pisupati S V. A review of thermal co-conversion of coal and biomass/waste. Energies, 2014, 7: 1098-1148.

[5] Ibitoye S E, et al. An overview of biochar production techniques and application potentials in the iron and steel industry. International Journal of Coal Science & Technology, 2024, 11: 74.

[6] Cheng Z, Zhao Y, Chou K C, et al. Characteristics of charcoal combustion and its effects on iron ore sintering performance. Applied Energy, 2016, 161: 364-374.

[7] Niesler M, Stecko J, Stelmach S, et al. Biochars in iron ores sintering process: effect on sinter quality and emission. Energies, 2021, 14: 3749.

[8] Wang J, et al. Effect of biochar substitution on iron ore sintering process and sinter quality: a review and new evidence. Journal of Environmental Management, 2023, 345: 118947.

[9] Li X, Hu S, Xiang J, et al. Catalytic reduction of NO using iron oxide impregnated biomass and lignite char for flue gas treatment. Fuel Processing Technology, 2016, 148: 91-98.

[10] Wang Y, Jiang L, Hu S, et al. Evolution of structure and activity of char-supported iron catalysts prepared for steam reforming of bio-oil. Fuel Processing Technology, 2017, 167: 180-190.

[11] Min Z, Yimsiri P, Asadullah M, et al. Char-supported iron catalysts for tar destruction during gasification. Fuel, 2014, 117: 708-715.

[12] Pu Y, Zhang X, Liu H, et al. Experimental study of synergistic effects on the combustion behavior of biomass and coal blends. Journal of the Energy Institute, 2024, 117: 101442.

[13] Khajeh A, et al. Effects of various carbon-supported iron catalysts on tar reforming and syngas production. Journal of Cleaner Production, 2023, 389: 136022.

[14] Hu S, Xiang J, Sun L, et al. Role of iron species in char-supported catalysts during tar reforming and char activation. Fuel, 2014, 134: 208-215.

[15] Zhao Z B, Li W, Li B Q. Catalytic reduction of NO by coal chars loaded with Ca and Fe in various atmospheres. Fuel, 2002, 81: 1559-1564.

[16] Illan-Gomez M J, Linares-Solano A, Radovic L R, et al. NO reduction by activated carbon. Catalytic effect of iron species. Energy & Fuels, 1996, 10: 158-168.

[17] Lei Z, Wang Y, Zhang L, et al. Catalytic combustion of coke and NO reduction in situ by Fe-CaO catalyst in iron ore sintering. Energy, 2021, 216: 119246.

[18] Lei Z, Wang Y, Zhang L, et al. Catalytic combustion of coke nuts and in-situ NO reduction in iron ore sintering by composite catalyst. Fuel, 2021, 289: 119800.

[19] Zhao J P, Lu L, Holmes R J. Modelling fuel combustion in iron ore sintering. Applied Mathematical Modelling, 2015, 39: 1845-1859.

[20] Wang Y, Zhang L, et al. Numerical simulation on the effects of co-injection of alternative fuels in blast furnace raceway. Fuel, 2023, 343: 127999.

[21] Zhao P, Wang H, et al. Numerical simulation research on the co-combustion of biochar and pulverized coal in the raceway of blast furnace. Energy, 2025, 319: 133520.

[22] Kieush L, et al. Utilization of torrefied biomass in steel production. Metals, 2022, 12: 2005.

[23] Garcia-Garcia A, Illan-Gomez M J, Linares-Solano A, Salinas-Martinez de Lecea C. Role of iron species in NO reduction by activated carbon. Carbon, 1998, 36: 613-620.

[24] Tan W, et al. Toward carbon emission reduction in steel production by using biomass and biochar. ACS ES&T Engineering, 2024, 4: 1087-1110.

[25] Niesler M, Kwiecinska-Mydlak A, Stelmach S, et al. Pilot and semi-industrial evaluation of residual biomass char as a substitute for coke breeze in sintering. Energies, 2021, 14: 3749.

[26] Bazaluk O, et al. Metallurgical coke production with biomass additives. Materials, 2022, 15: 1234.

[27] Qi X, et al. Experimental study of the catalytic effect of iron on low-rank coal gasification reactivity. ACS Omega, 2022, 7: 36115-36125.

[28] Wang J, et al. Exploring the effect of precursor materials on Fe-loaded biochar catalyst performance. Bioresource Technology, 2024, 392: 130042.

[29] Yuan Y, Li C, Wang H, et al. Co-combustion characteristics of typical biomass and coal blends and kinetic analysis. Frontiers in Energy Research, 2021, 9: 753622.

[30] Zhang R, Chen L, Li Y, et al. Combustion characteristics and synergy behaviors of biomass and coal under oxy-fuel conditions. Science China Technological Sciences, 2018, 61: 1722-1732.

[31] Soleh M, et al. Impact of different kinds of biomass mixtures on combustion performance and synergy in coal cofiring. Clean Energy, 2023, 7: 1136-1149.

[32] Poomsawat S, et al. Investigation of co-combustion characteristics and kinetics of lignite and manure blends. Case Studies in Thermal Engineering, 2024, 59: 104499.

[33] Han T, Hu C, Shi X. Coke breeze combustion and emission behaviors of CO and NO during iron ore sintering. SSRN preprint, 2024. DOI: 10.2139/ssrn.4854756.

[34] Xu C, Liu X, Wang Y, et al. Structure characteristics and combustion kinetics of the co-pyrolytic char from coal gangue and biomass. Scientific Reports, 2024, 14: 11392.

[35] Eckhard T, et al. Catalytic effect of iron and alkali/alkaline earth metal sulfates on biomass char conversion. Energies, 2023, 16: 4884.

[36] Yang J, Mestl G, Herein D, et al. Reaction of NO with carbonaceous materials. Part 1: reaction and adsorption of NO on ashless carbon black. Carbon, 2000, 38: 715-727.

[37] Javed M T, Gibbs B M, Nimmo W, et al. Effect of catalysts on NO reduction during reburning with coal chars as the fuel. Fuel, 2007, 86: 2680-2688.

[38] Zhao J, Zhang L, Zhou M, et al. Modelling and analysis of combustion behaviour of granulated fuel particles in iron ore sintering. Powder Technology, 2019, 356: 424-435.

[39] Kumar S, et al. Catalytic influence of iron oxide (Fe2O3) on coal pyrolysis and char combustion. Results in Engineering, 2024, 23: 102462.

[40] Daood S S, Javed M T, Gibbs B M, et al. NOx reduction, combustion efficiency and fly ash properties of coal/biomass co-combustion in air and oxy-fuel conditions. Fuel, 2014, 132: 193-200.

[41] Saikaew T, Supudommak P, Pattiya A. Emission of NOx and N2O from co-combustion of coal and biomass in a fluidized-bed combustor. International Journal of Greenhouse Gas Control, 2012, 6: 23-33.

[42] Yang Y, et al. Biomass ash chemistry in oxygen carrier aided combustion. Fuel, 2024, 358: 129797.

[43] Rasaq W A, et al. Catalyst-enhancing hydrothermal carbonization of biomass: a review. Biochar, 2024, 6: 28.

[44] Lee D G, et al. Combustion visualization analysis of alternative fuels in the raceway for iron production. Heliyon, 2024, 10: e25196.

[45] Zhang L, Lei Z, et al. Steel scale-CaO composite catalyst for coke combustion and simultaneous SO2/NO reduction. International Journal of Minerals, Metallurgy and Materials, 2022, 29: 1802-1812.

[46] Ma C, et al. Experimental investigation on the effect of iron-rich coal ash on biomass combustion performance in CFB boilers. Energy, 2025, 315: 132808.

[47] Niu Y, et al. Advancements in biomass gasification research utilizing iron-based oxygen carriers. Journal of the Energy Institute, 2024, 117: 101455.

[48] Gholizadeh M, et al. A review on thermochemical based biorefinery catalyst development for biomass valorization. Sustainable Energy & Fuels, 2023, 7: 3852-3883.

[49] Feng D, et al. Effect of biochar support on the catalytic performance of Fe-based catalyst for methane decomposition. Fuel Processing Technology, 2023, 246: 107796.

[50] Li L, et al. Fe-rich biomass-derived char for microwave-assisted CO2 reforming of methane. Science of the Total Environment, 2019, 669: 434-443.

[51] Liu N, et al. Co-pyrolysis behavior of coal and biomass: synergistic effect and mechanism. Processes, 2024, 12: 141.

[52] Zhang W, et al. Co-gasification of coal and biomass: synergistic effects on reactivity and mechanism. Energy Sources Part A, 2024, 46: 2357222.