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Research progress on influencing factors and control methods of slagging in biomass combustion

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Biomass combustion serves as a carbon-neutral energy solution but faces persistent challenges due to ash-related operational inefficiencies. This review systematically examines the thermochemical interactions among alkali metals (K, Na), chlorine (Cl), and sulfur (S) in biomass ash systems, elucidating their synergistic contributions to deposition mechanisms while evaluating mitigation approaches. KCl volatilization-condensation dominates in high-chlorine feedstocks (agricultural residues), whereas sulfates control ash deposition in lignocellulosic biomass. Bed agglomeration mechanisms stem from alkali silicate eutectics with depressed melting points ($K_2O \cdot nSiO_2$), while chloride-induced degradation of protective oxide layers initiates metallic corrosion. Comprehensive assessment of mitigation techniques reveals aluminosilicate additives (kaolin) outperform conventional pretreatment methods (aqueous and acid leaching), achieving ash fusion temperature elevation beyond 1,300°C through interfacial reactions generating refractory kalsilite ($KAlSiO_4$). The synthesis demonstrates that hybrid strategies combining fuel-specific preprocessing with optimized additive formulations produce synergistic mitigation effects. These insights provide mechanistic understanding essential for optimizing combustion system durability, while highlighting unresolved challenges in fuel-additive compatibility, additive stability under thermal cycling, and advanced corrosion-resistant material development.

KEYWORDS

biomass combustion, biomass ash, slagging, alkali metals, ash behavior control

1 Introduction

The imperative to achieve carbon neutrality under intensifying climate change has positioned biomass combustion as a critical transitional technology, with potential to displace 8.2 GtO₂-equivalent annual emissions from fossil fuels. However, its sustainable implementation faces dual environmental constraints: combustion-generated particulate emissions (PM_{2.5}: 2.1–5.3 g/kg, PM₁₀: 3.8–7.6 g/kg) and carbon monoxide (18–47 g/kg) exacerbate atmospheric pollution, while intrinsic ash behavior—particularly alkali-induced slagging—compromises 12%–18% of combustion efficiency in industrial systems (Huang et al., 2024; Kim et al., 2024). This operational paradox underscores the necessity to resolve ash transformation mechanisms, where potassium-silicate interactions dominate slag formation in agricultural residues (slagging indices >0.8), contrasting with sulfate-controlled deposition in woody biomass. Such fundamental limitations not only challenge emission reduction commitments but also hinder the technology's scalability under Net-Zero scenarios. As a major agricultural country, China possesses abundant

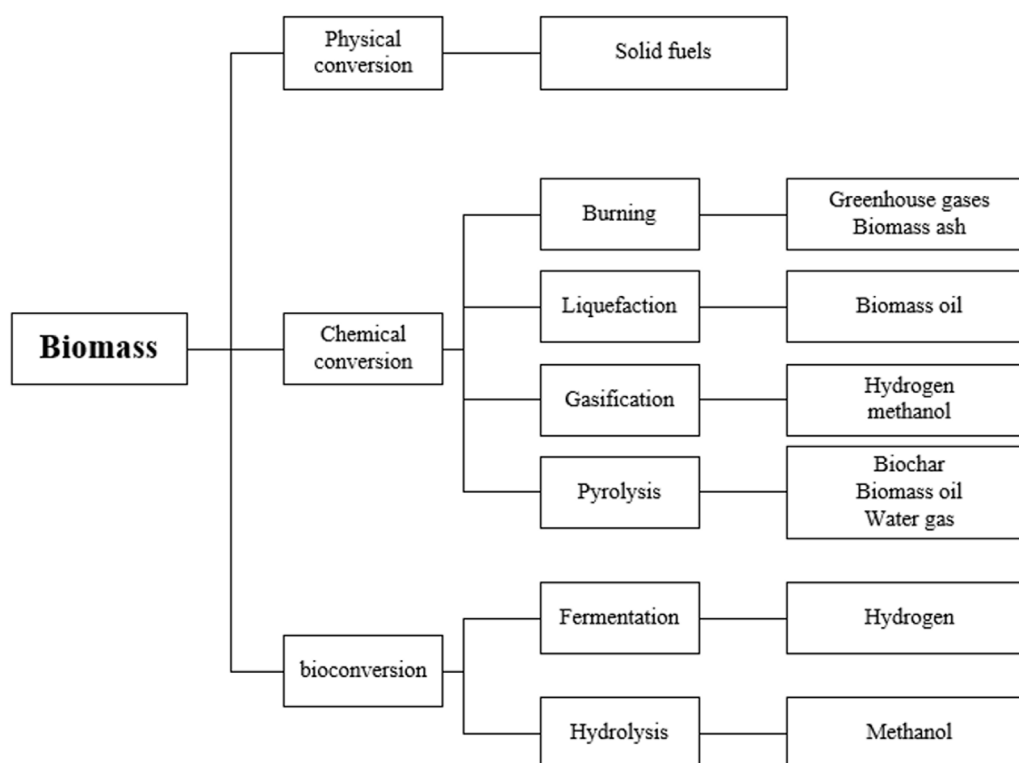


FIGURE 1
Biomass conversion technology and products.

agricultural straw resources, particularly from corn, wheat, and rice—the three predominant contributors to national straw supply (Antar et al., 2021). These resources are predominantly utilized through three principal pathways: domestic fuel provision, agricultural fertilization, and industrial feedstock applications. Direct combustion has emerged as an effective strategy for large-scale biomass utilization, yet the characteristic high chlorine and alkali metal content inherent in Chinese crop straw induces significant technical challenges, including heat exchange surface deposition and high-temperature slagging during combustion processes. Current research efforts primarily concentrate on three technological pathways: biomass gasification, combustion, and pyrolysis (Figure 1).

Biomass resources are formally defined as heterogeneous organic substrates originating from photosynthetic conversion of atmospheric CO₂, serving as renewable feedstocks for energy production and biorefinery applications (Sukatits, Wee, and Aris 2022). Based on provenance and physicochemical characteristics, they are systematically categorized into four classes: (1) Woody biomass comprising forestry residues (e.g., bark, branches), silvicultural byproducts (e.g., sawdust, wood chips), and post-consumer timber; (2) Agricultural biomass including lignocellulosic crop residues (e.g., cereal straws, rice husks), dedicated energy crops (e.g., *Miscanthus*, switchgrass), and agro-industrial processing wastes (e.g., sugarcane bagasse); (3) Waste-derived biomass encompassing municipal solid organic fractions, wastewater treatment biosolids, and construction/demolition cellulose-rich debris; (4) Animal-derived biomass consisting of livestock

manures, anaerobic digestion effluents, and slaughterhouse residues (Guo et al., 2024; Alami et al., 2021). These carbonaceous materials exhibit near-carbon-neutral characteristics when utilized in energy systems, as photosynthetic carbon sequestration during growth phases counterbalances subsequent thermochemical conversion emissions. Strategic advantages stem from their global distribution scalability, biomass can play two roles, namely, bio-carbon capture and storage/bio-carbon capture and storage, and compatibility with circular bioeconomy frameworks through cascaded utilization pathways (Ilmiawati et al., 2025).

Biomass is composed of 38%–50% cellulose, 23%–32% hemicellulose, 15%–25% lignin, and 5%–13% other components (e.g., inorganic species and extracts) (Table 1) (Li et al., 2025). Its elemental composition is dominated by carbon (C), hydrogen (H), and oxygen (O), with carbon (approximately 50%) and oxygen (around 40%) together accounting for over 90% of its dry material. Slagging, ash accumulation, and slagging in biomass combustion systems can be attributed to intricate interactions between design parameters (e.g., thermal gradients and gas flow dynamics) and the unique physicochemical characteristics of the fuel (Su et al., 2024). In addition, biomass contains trace quantities of minerals, either in ionic form or as chemical compounds, such as aluminum (Al), calcium (Ca), iron (Fe), magnesium (Mg), sodium (Na), potassium (K), phosphorus (P), sulfur (S), and silicon (Si). At a structural level, hemicellulose and lignin form a chemically bonded matrix that encapsulates cellulose. Most of the ash-forming constituents are chiefly concentrated within the three-dimensional network of lignin. In comparison, the existence of major mineral elements results in ash

TABLE 1 The conventional contents of cellulose, hemicellulose and lignin in biomass.

Component	Percentage	Composition characteristics
Cellulose	38-50	The high-molecular-weight glucan formed by the β -1,4-glycosidic linkages connecting glucose molecules has stable chemical properties and is not prone to decomposition
Hemicellulose	23-32	A polysaccharide composed of monosaccharides such as D-xylulose, L-arabinose, D-galactose and D-mannose. Its molecular weight is lower than that of cellulose and it is relatively easy to hydrolyze into basic sugars
Lignin	15-25	A three-dimensional, non-crystalline and highly branched aromatic polymer composed of structural units derived from o-benzyl phenol or its derivatives

fouling and slagging towards process equipment. In the combustion process, basic metal oxides participate in complex combustion reactions and eventually form silicates, chlorides and sulfates. These compounds can be mixed with other metal oxides to form low-temperature stable blends. Then alkali earth metals may also react with or dissolve into the melt K-silicates (Bostrom et al., 2012).

Biomass feedstock ash composition and its physicochemical attributes—especially the levels of alkali/alkaline earth metals (AAEMs), chlorine (Cl), and silicon-sulfur compounds—serve as critical determinants of combustion efficiency and operational reliability. The rapid release of volatiles from biomass, coupled with the intermittent feeding of biomass fuels and uneven spatial distribution of fuel particles, leads to inconsistency between the timescales of chemical reactions and diffusion. This results in inadequate mixing of fuel and oxygen, thereby reducing combustion efficiency (Ma et al., 2025). In particular, AAEMs (e.g., potassium, sodium, and calcium) combined with chlorine lower ash fusion temperatures through eutectic interactions, whereas silicon-sulfur compounds (such as $\text{SiO}_2\text{-SO}_3$ complexes) intensify ash agglomeration. Collectively, these constituents are recognized as key drivers of the interconnected processes leading to slagging, fouling, and high-temperature slagging, thereby prompting the development of novel material and process solutions (Yao et al., 2020). Operational challenges related to ash manifest via four primary mechanisms: slagging induced by alkali metals, agglomeration from silicate melts, particulate deposition dynamics, and slagging mediated by chlorine. Furthermore, elevated concentrations of chlorine and alkali metals (notably K and Na) in combustion environments intensify ash deposition, while the low melting points of alkali metal compounds facilitate particle adhesion and bonding (Tiainen, Daavitsainen, and Laitinen 2002). Under elevated thermal conditions, alkali metals and their derivatives follow two distinct migration routes: one involving direct deposition onto furnace surfaces via inertial impaction, and another characterized by vapor-phase transport with subsequent heterogeneous condensation onto downstream heat-exchanger surfaces, forming submicron fly ash particles. Addressing the complex multiphase evolution of biomass ash remains a significant obstacle to expanding clean energy systems. Figure 2 illustrates the trend in publications over the past 5 years focusing on biomass for diverse applications, thereby highlighting its emerging potential and growing scholarly attention. Biomass combustion technology-an essential pillar of decarbonization strategies-has garnered significant interest owing to its sustainable feedstock foundation and carbon-neutral life cycle. However, large-scale industrial deployment is impeded by

persistent operational challenges, including slagging, fouling, and high-temperature corrosion. These issues stem from the migration, transformation, and interactions of alkali metals, chlorine, and sulfur, which collectively govern the dynamics of ash fusion and deposition. Although previous studies have partially unraveled ash evolution pathways, high ash containing biomass demonstrates several challenges when applying it as a biofuel owing to the increase in the capital and operating costs (Hess et al., 2019). Biological co-combustion, leaching, and adding additives have been identified as the most effective deashing treatment methods.

This review is to systematically elucidate the thermochemical interactions of alkali metals, chlorine, and sulfur in biomass ash systems and their roles in slagging mechanisms. Additionally, it evaluates mitigation strategies, including leaching pretreatments and aluminosilicate additives, to address ash-related operational challenges. By clarifying the slagging mechanisms and quantify alkali metal migration pathways, this advances the optimization of biomass combustion systems for enhanced durability and efficiency. The review provides a foundation for developing scalable solutions to mitigate ash deposition and corrosion, thereby supporting sustainable biomass energy integration into decarbonization frameworks.

2 Biomass ash and mechanism of slagging

In the process of biomass energy utilization, biomass ash is an important factor affecting the utilization process. Due to the high content of alkali metals, alkaline earth metals and chlorine in biomass fuel, After the alkali metal sulfate, chloride, carbonate and silicate enter the gas phase successively, they condense on the surface of fly ash particles, which reduces the melting point of fly ash and increases the viscosity of fly ash. Under the action of the air flow in the furnace, they bond on the heating surface and form the slag (Werkelin et al., 2010).

Figure 3 illustrates the processes of ash generation and modification during biomass combustion. Biomass combustion (Jia and Lighty 2012; Dai et al., 2025), volatile organometallic species (e.g., chromium [Cr] and vanadium [V]) are initially released during the ignition of biomass particles and the subsequent formation of char. Thereafter, alkali and alkaline earth metals—specifically potassium (K), sodium (Na), and calcium (Ca)—along with trace volatile elements such as mercury (Hg), arsenic (As), and selenium (Se), are liberated through surface diffusion from the char

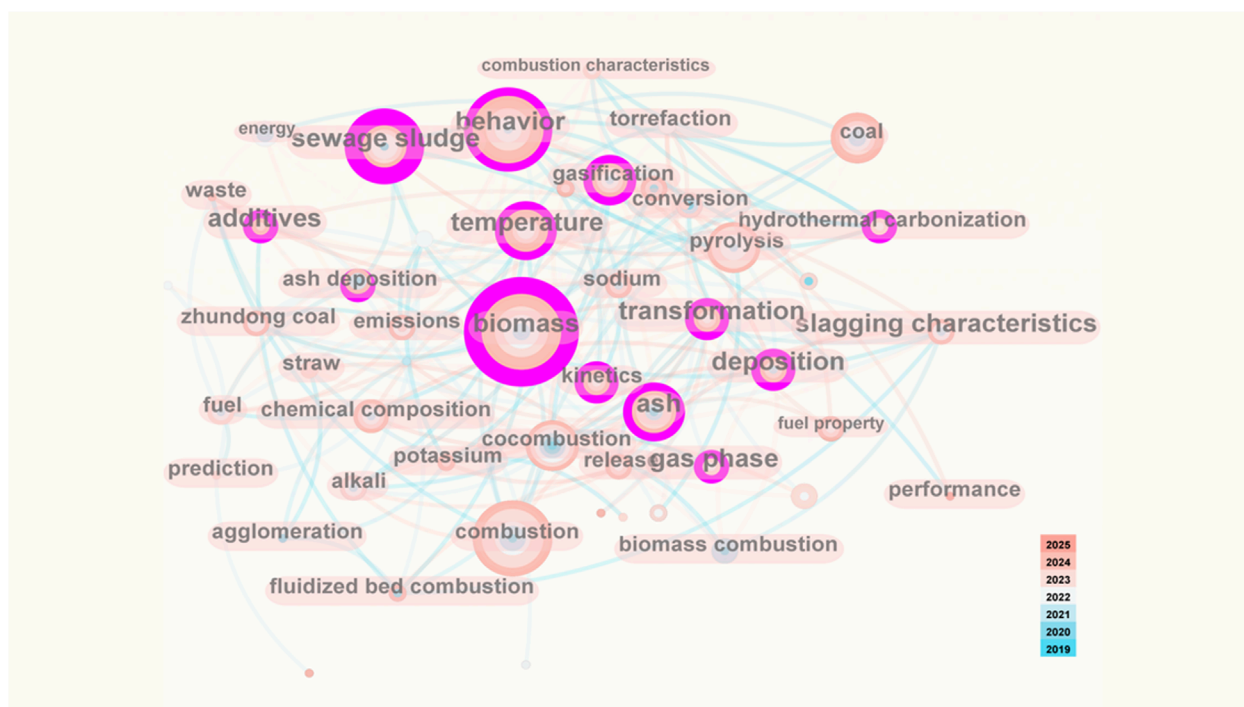


FIGURE 2
Representation of bibliometric analyses of words in relation to research on the use of biomass as a substrate in various applications, based on data obtained from the Scopus database between 2019 and 2025 using the Citespace program.

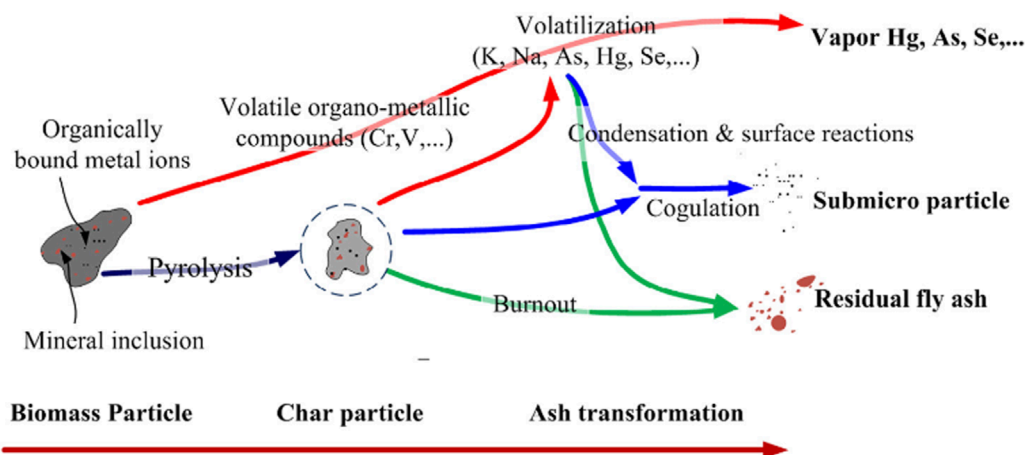


FIGURE 3
Formation and transformation mechanism of ash in biomass combustion process (Jia and Lighty 2012) Copyright © 2012 American Chemical Society.

matrix. When the gas-phase temperature declines, these compounds undergo nucleation, resulting in the production of submicron aerosol particles via gas-to-particle conversion. Additionally, a portion of these volatiles condenses onto the surfaces of the residual fly ash. Elevated levels of alkali metals, particularly potassium (K), precipitate ash-related operational challenges, including high-temperature corrosion and slagging phenomena, owing to the synergistic interplay between nucleation-condensation processes and secondary chemical reactions.

2.1 Potassium (K) and sodium (Na)

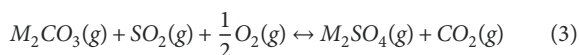
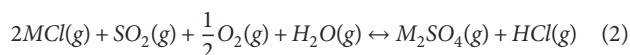
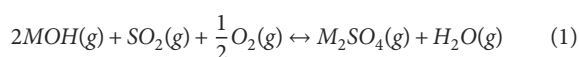
Alkali metals (lithium (Li), sodium (Na), potassium (K), rubidium (Rb), cesium (Cs), and francium (Fr)) are defined by an ns^1 configuration in their s orbital and are classified as Group 1 elements on the periodic table. These metals exhibit distinct properties, including high chemical reactivity, notable luster, and relatively low mechanical strength at ambient temperature, a behavior attributed to their minimal ionization energies. In biomass ash, sodium

and potassium are particularly prevalent due to their superior mobility, serving as principal agents in adverse processes such as aerosol generation and slag accumulation. During the thermal decomposition of biomass, alkali metals volatilize, producing gas-phase precursors that nucleate into particulate compounds—such as KOH, KCl, K₂SO₄, NaCl, and Na₂SO₄ through gas-solid transformation mechanisms. These formed aerosol particles promote ash agglomeration by means of surface condensation and chemical bonding, ultimately facilitating slag formation via eutectic interactions in high-temperature regions (Mlonka-Medra et al., 2020).

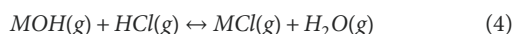
The thermochemical processing of biomass fuels initiates intricate alkali metal (K/Na) speciation dynamics and migration routes, driven by pyrolytic degradation of lignocellulosic polymers (lignin, cellulose, hemicellulose). Release behavior varies markedly with feedstock characteristics: (1) Low-chlorine biomass (e.g., woody types): Alkali metals primarily volatilize into stable sulfates (K₂SO₄, Na₂SO₄) and aluminosilicates (KAlSi₃O₈), facilitated by sulfur-silicate interactions; (2) High-chlorine biomass (e.g., herbaceous/straw feedstocks): Alkali species form volatile chlorides (KCl, NaCl) via chlorine-mediated coordination, with straw-derived fuels releasing substantial gaseous KCl/NaCl at elevated temperature (Wei, Schnell, and Hein 2005). Within the intermediate temperature, chloride-sulfate conversion occurs through gas-phase interactions between alkali chlorides and sulfur oxides (SO₂/SO₃) present in combustion effluents. Resulting sulfates undergo homogeneous nucleation to generate submicron aerosols (<1 μm), which subsequently condense on heat exchanger surfaces via thermophoretic forces.

Despite high alkali concentrations, chlorine-deficient woody biomass generates gaseous hydroxides (KOH, NaOH) during thermal degradation. During effluent cooling, these hydroxides participate in heterogeneous reactions with sulfur oxides to yield sulfates, while inherent silicates (e.g., SiO₂) catalyze nucleation, amplifying aerosol production. Alkali species adsorb onto fly ash particulates during gas-to-particle transitions, markedly reducing ash fusion temperatures (AFT) and elevating surface viscosity by two to three logarithmic units (Wang et al., 2008; Chen et al., 2024). Turbulent flow conditions promote collisions among viscous particles, leading to stratified slag accumulation on heat exchanger surfaces. These processes are thermodynamically regulated by the equilibria outlined in Equations 1–5 (Blomberg 2011; Thy et al., 2006), where M represents alkali or alkaline earth metals.

Sulfation reaction:



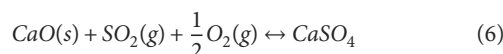
Chlorination reaction:



2.2 Calcium (Ca) and magnesium (Mg)

Group IIA elements (Be, Mg, Ca, Sr, Ba, Ra), termed alkaline earth metals, display lower reducing capacity relative to alkali metals at ambient conditions (25°C, 1 atm), a property governed by their ns² valence configuration. These elements exist as lustrous metallic solids characterized by elevated ionization energies. Analyses of biomass ash composition reveal that Ca and Mg constitute over 90% of alkaline earth metal mass fractions (Yu et al., 2021), a pattern stemming from their abundance in organic matrices (e.g., calcium pectate bonds in plant cell walls) and the superior thermal resilience of their mineralized forms. Under combustion conditions, these metals preferentially form thermally stable crystalline structures. Such refractory phases increase ash fusion temperatures while suppressing the generation of low-melting alkali silicates via competitive ion exchange mechanisms (Lindstrom et al., 2007).

As the predominant mineral constituent in woody biomass, calcium manifests in three primary configurations: organically chelated, acid-leachable, and acid-resistant. Acid-resistant calcium, primarily sequestered in aluminosilicate matrices, demonstrates thermal resilience surpassing common combustion range, thus minimally impacting gaseous pollutant evolution mechanisms. Conversely, organically chelated and acid-leachable calcium species decompose via decarboxylation under pyrolytic conditions, yielding nanoscale CaO particles that actively engage in heterogeneous interactions within combustion chambers and effluent streams. These CaO nanoparticles promote SO₂ sulfation through chemisorptive pathways, as quantified in Equation 6 (Niu, Tan, and Hui 2016). CO₂ and SO₂ competitively adsorb onto CaO surfaces, producing passivating carbonate-sulfate surface films that suppress alkali chloride sulfation. This phenomenon amplifies the deposition likelihood of unreacted chlorides on thermal exchange interfaces, intensifying fouling and corrosion hazards.



2.3 Sulfur (S), chlorine (Cl) and phosphorus (P)

Non-metallic elements, such as sulfur (S), chlorine (Cl), and phosphorus (P), are characterized by properties including low atomic density, high electronegativity, and limited electrical conductivity. They play a crucial role in directing the formation routes of gaseous pollutants during biomass combustion. For example, Capablo et al. measured chlorine and sulfur contents across various biomass feedstocks, encompassing agricultural residues (e.g., brewery spent grains with 0.01 wt% Cl and 0.22 wt% S), forestry residues (e.g., empty fruit bunches with 0.35 wt% Cl and 0.13 wt% S), and municipal waste biomass (e.g., shea waste with 0.24 wt% Cl and 0.13 wt% S) (Capablo et al., 2009). Although present in trace amounts (<1 wt%), these elements exert a disproportionate influence on the kinetics of thermal decomposition and the emission profiles of pollutants. In biomass

fuels, sulfur primarily occurs as inorganic sulfate species (SO_4^{2-}) and heterocyclic organosulfur compounds; during combustion, these compounds decompose thermally to yield sulfur dioxide (SO_2) in the gas phase. This transformation promotes the formation of acid rain precursors and particulate matter, underscoring the environmental significance of sulfur speciation in combustion systems (Niu et al., 2013). Conversely, chlorine mainly exists in water-soluble chloride forms (e.g., KCl, NaCl) in biomass feedstocks; these chlorides volatilize during combustion to generate gaseous alkali metal chlorides (KCl(g) and NaCl(g)) (Bostrom et al., 2012). The volatile chlorides then participate in both homogeneous and heterogeneous reaction pathways, as detailed in Equation 3, thereby contributing to corrosive deposit formation and the development of secondary aerosols. Moreover, Blasing et al. identified phosphorus as a critical non-metallic trace element in biomass, with measurable levels in lignocellulosic feedstocks such as willow, poplar, oak, and lignocellulose-rich residues (e.g., pine seed husks, hazelnut shells, and almond shells) (Blaesing, Zini, and Mueller 2013). Notably, even minor chlorine contents can intensify ash slagging, with slagging severity showing a strong positive correlation with chloride concentration due to the formation of low-melting-point eutectic mixtures. This observation underscores the essential role of chlorine speciation in feedstocks for mitigating combustion-related fouling and slagging.

3 Principle of slagging in biomass combustion

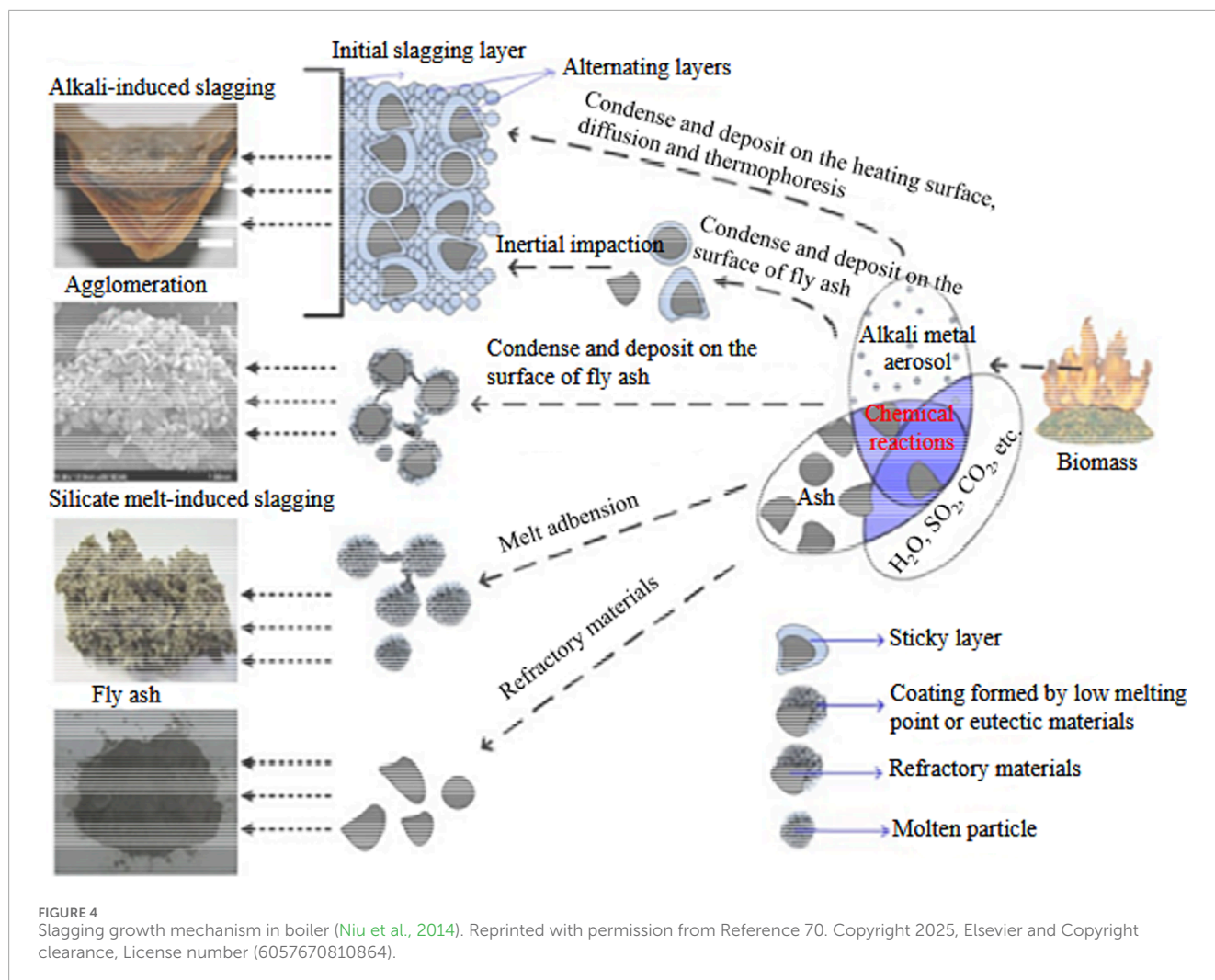
Although both slagging and fouling represent ash deposition processes in biomass boiler flue gas systems, they operate via fundamentally different mechanisms and are influenced by varying temperature regimes. Slagging manifests in high-temperature regions (above 1,000°C) via viscous flow sintering of molten ash, a process propelled by the phase transformation of alkali-rich silicates and aluminosilicates. Conversely, fouling prevails in lower-temperature areas (below 800°C) through the dry deposition of unmolten particulate ash (Shao et al., 2012). The unmolten ash is defined by a melting point that considerably exceeds the temperature of the deposition surface. Such deposits undermine the efficiency of slag removal, diminish thermal performance, and markedly curtail the operational lifespan of the boiler (Indrawan et al., 2020; Corona et al., 2020). Compared to coal-fired boilers, biomass systems exhibit a greater susceptibility to slagging and fouling, attributable to their elevated levels of alkali metals and chlorine (Rong et al., 2017). Chlorine promotes the volatilization of potassium as KCl vapors, which subsequently condense into submicron aerosols. These aerosols then deposit by means of thermophoresis—a migration driven by temperature gradients—and inertial impaction, ultimately forming tenacious layers on the surfaces of convective passes.

One study found that the K, S and Cl of biomass fuel gradually decreased with the temperature rising to 1,200°C, and their ash content also gradually decreased (Johansen et al., 2011). Then they remain either unchanged or decrease slightly between 1,200°C and 1,400°C. Cl concentration is essentially zero at 815°C. However, between 815°C and 1,200°C, K concentration

decreases because of the volatility of KOH and K_2SO_4 aerosols. Meanwhile, inorganic S is released in the form of SO_2 by the decomposition of K_2SO_4 . All these conditions result in the continuing decrease of the ashing ratio as temperature increase until 1,200°C.

Deposits on the walls of tubes emerge from both solid-phase mineral conversions and vapor-phase condensation processes. The resulting layers, typically rich in alkali sulfates (such as K_2SO_4) and chlorides (such as KCl), possess adhesive qualities attributable to their low eutectic melting temperature, thereby fostering secondary agglomeration through capillary forces. Controlled drop-tube furnace experiments conducted by Wang et al. demonstrated that a synergistic interaction between sulfate and chloride compounds critically influences ash deposition kinetics in biomass combustion systems. At combustion temperatures exceeding 800°C–900°C, gaseous KCl participates in heterogeneous gas-solid reactions with SO_2 (Wang L. et al., 2012).

When flue gas temperatures drop below 500°C, thermophoretic effects combined with turbulent diffusion drive the condensation of alkali-enriched aerosols, thereby initiating the formation of a sticky slag layer on heat exchange surfaces. This viscous film subsequently augments the adherence potential for additional particulate deposits. A portion of these alkali aerosols condenses onto fly ash particles, either creating tacky surfaces or reacting with refractory oxides to produce eutectic mixtures with melting points below 700°C. Upon further reduction of the gas temperature to below 300°C, alkali vapors traverse a sequence of phase changes: an initial phase (comprising condensation, nucleation, and coalescence) yields submicron aerosols (less than 1 μm), whereas a secondary phase, marked by oxidation, re-nucleation, and coalescence, produces coarser fly ash particles (greater than 10 μm) (Bostrom et al., 2012). Irrespective of their surface viscosity, coarse particles predominantly deposit onto the primary slag layer via inertial impaction. In contrast, fine particles enriched with potassium, sodium, chlorine, and sulfur (e.g., KCl, $\text{K}_3\text{Na}(\text{SO}_4)_2$) tend to concentrate on surfaces due to their elevated surface-to-volume ratios, thereby enhancing the adsorption of silicon- and aluminum-rich coarse particles through electrostatic and van der Waals interactions (Nordgren et al., 2013). The lower adhesion efficiency between fine and coarse particles triggers secondary enrichment processes, ultimately producing self-organized, stratified slag formation via a hierarchical deposition mechanism. This process elucidates the heterogeneous microstructure characteristic of combustion deposits in industrial biomass boilers. In summary, the initial slag layer is composed of fine ash particles alongside coarse particles that display only partial adhesion. Owing to the surface's low operational temperature and substantial thermal resistance, the layer remains non-adhesive even as its temperature approaches, but does not exceed, the ash fusion point. When ash-laden flue gas impinges upon the slag layer, inertial forces facilitate the primary deposition of particles that are softened or partially molten. As the slag layer accumulates, its surface temperature eventually exceeds the melting threshold, thereby transitioning into a molten state. Thereafter, fly ash particles coalesce to form a dense coke layer through secondary deposition. Gravitational shedding occurs when the deposit's weight overcomes its structural cohesion or adhesion to the furnace wall (Zhou et al., 2013; Liu et al., 2011). Ultimately, the interplay



between layer accumulation and gravitational shedding establishes a dynamic equilibrium that stabilizes the deposit thickness (Figure 4) (Niu et al., 2014).

4 Biomass ash control methods

The application of high-ash biomass in thermochemical combustion systems poses significant technical and economic barriers, stemming from elevated capital expenditure and operational expense linked to ash management, accelerated equipment degradation, and unplanned maintenance interruptions (Hess et al., 2019). Three principal approaches-co-processing with low-ash feedstocks, leaching processes (e.g., water or acid pretreatment to diminish alkali concentrations), and additive integration (e.g., aluminosilicates to sequester mobile alkali species) have demonstrated efficacy in addressing ash-related inefficiencies. Selecting the optimal methodology necessitates a comprehensive evaluation of feedstock-specific ash composition (e.g., alkali metals, chlorine, silica ratios), ash production rates, regulatory limitations (e.g., particulate emission thresholds), and site-dependent

variables, including reactor design and operational adaptability (Bostrom et al., 2012).

4.1 Blend combustion

Biomass fuels are characterized by elevated alkali metal content, which induces molten ash formation under high-temperature conditions. This phenomenon facilitates slag deposition on heat exchange surfaces and exacerbates corrosion at elevated temperatures. Co-combustion, the integrated utilization of biomass with complementary fuels for energy generation, has emerged as a viable approach for large-scale waste management and direct energy recovery (Aziz, Budianto, and Oda 2016; Khalid et al., 2024). This method not only diminishes waste stockpiles but also facilitates energy extraction. Relative to mono-fuel combustion, it substantially reduces the release of pollutants into the atmosphere (Rong et al., 2017). Han J (Han et al., 2023) found that have investigated blending biomass with municipal sludge and select coal varieties (e.g., high-calcium coal), revealing that such mixtures minimize ash agglomeration during thermal conversion. Table 2 summarizes documented applications of co-combustion systems addressing

TABLE 2 Co-combustion serves as a strategic solution to mitigate ash.

Biomass (Targeted)	Biomass (regulator)	Major finding	Ref.
Wheat straw	Paper making sludge	(1) Increase in ash melting temperatures of straw pellets (2) At 20% and above weight proportion of sludge addition, no occurrence of sintering and slagging was observed	Matus et al. (2018)
Wheat straw pine	sewage sludge	(1) Pine sawdust enhanced sludge combustibility by lowering ignition temperature and improving efficiency. while effectively immobilizing heavy metals (Cr, Ni, Zn, Cu) in ash residues and reducing volatilization (2) Compared to wheat straw, pine sawdust exhibited superior heavy metal fixation capacity	Shen et al. (2025)
Corn straw	high-Ca coal	The co-combustion of high-calcium coal significantly reduced the slagging rate of ash, lowering the ash slagging rate by 17%–65%. This is because the calcium in the silicate/alumino-silicate replaces the base, inhibiting the agglomeration and sintering of ash particles, ultimately reducing the inert impact and capture of ash particles on the pipeline	Han et al. (2023)
Bark of sugi Sakura	Bituminous coal	(1) Increasing high-ash biomass (bark of sugi) ratio (30%–70%) shifts dominant minerals from calcium aluminosilicates (anorthite/gehlenite) to calcium silicates (pseudo wollastonite/rankinite/ α -Ca ₂ SiO ₄). Calcium-rich minerals and their eutectic mixtures (e.g., pseudo wollastonite-anorthite-gehlenite system, eutectic point 1,267°C) substantially reduce ash melting temperatures to 1,200°C–1,300°C (vs pure coal ash ~1,500°C) (2) High-ash biomass (bark of sugi) co-firing exacerbates slagging risks due to calcium mineral eutectics, advocating low-ash biomass (sakura) utilization for sustainable pulverized coal boiler operation	Priyanto et al. (2016)
Processed into refuse-derived fuel (RDF)	Coal	(1) RDF exhibits higher slagging/fouling risks than coal due to Ca-rich minerals lowering ash melting points (2) Blends $\leq 10\%$ RDF mitigate slagging via Si/Al-dominated ash composition (clean probe at 600°C) (3) Higher ratios (15%–20%) intensify alkali-chloride synergy and Ca-based eutectic formation, elevating slagging/fouling propensity	Novendianto et al. (2024)
Acacia and mahogany wood	Coal	(1) Co-blending up to 40% woody biomass with coal poses medium-to-high ash deposition risks, evidenced by sintered ash spots on probes (2) Blended fuel (Acacia/Mahogany-coal) achieves 5,400–5,500 kcal/kg calorific value, reduces flue gas emissions, and offers cost-effectiveness for coal-fired power plants	Suyatno et al. (2025)

ash-related challenges. Suyatno, S (Suyatno et al., 2025) study found that biomass mixed fuel can reduce the risk of slagging, as well as improve the heating value. Research indicates that combining sewage sludge with biomass improves combustion performance while reducing ecological hazards, highlighting its technical viability (Wang et al., 2019). In light of operational limitations posed by ash-related issues in biomass-only systems, co-combustion represents a pragmatic strategy to avert equipment degradation. Analytical investigations highlight that synergistic effects arising from the interplay of biomass physicochemical characteristics improve

combustion behavior, offering insights for refining co-combustion protocols (Ni et al., 2022).

4.2 Washing

Washing pretreatment effectively mitigates ash-related challenges by leaching water-soluble ions (e.g., K^+ , Cl^- , SO_4^{2-}) from biomass, thereby suppressing the formation of low-melting alkali salts and eutectics during combustion (Tonn et al., 2012). Inorganic

species present in biomass can be divided into water soluble, acid soluble and residual compounds (Guo et al., 2020). Water soluble are salts which are easily soluble in water, e.g., alkali chlorides, alkali earth chlorides, sulfates and carbonates. Acid soluble are organically bound inorganic species and minerals that are indissoluble in water but soluble in acid, i.e., alkali earth carbonates, sulfates. Residual compounds are other acid indissoluble minerals. However, acid washing necessitates wastewater treatment to neutralize residual acidity and recover dissolved ions, adding operational complexity compared to water-only leaching.

4.2.1 Water washing

Water washing is commonly utilized in biomass pretreatment due to the high solubility of alkali metals (approximately 90%) and complete solubility of alkali chlorides in aqueous or acidic solutions (Wei et al., 2019). This process enhances fuel quality by preserving organic constituents, lowering ash content, and elevating calorific value. Such as, in the study (Singhal, Kontinen, and Joronen 2021) that the effect of water washing on fuel properties was evaluated, Washing was shown to have a high impact on the fuel properties and the fouling and slagging propensity. After washing, a significant increment in the content of VS ($\leq 5.2\%$), C ($\leq 1.8\%$), and O ($\leq 2.3\%$), and a slight improvement in HHVs (≤ 0.5 MJ/kg). Simultaneously, the high removal of ash ($\leq 39\%$), Cl ($\leq 87\%$), S ($\leq 74\%$), Mg ($\leq 71\%$), K ($\leq 68\%$), N ($\leq 46\%$), P ($\leq 45\%$), and Ca ($\leq 29\%$) was also noted. Thereby optimizing combustion performance. Furthermore, it efficiently extracts volatile components such as alkali metals, chlorine, and sulfur, which elevates ash fusion temperatures. These modifications mitigate operational challenges linked to biomass combustion, including particulate emissions, ash agglomeration, and slagging of equipment.

Gudka et al. reported that hot water leaching (85°C – 95°C) of wood pellets elevates the initial ash deformation temperature (IDT) from 820°C to $1,400^{\circ}\text{C}$, with potassium and sodium removal efficiencies ranging from 50%–90% and 10%–90%, respectively, contingent on feedstock porosity and treatment duration (Gudka et al., 2016). Carrillo et al. observed a 20% decrease in ash content and a 53% rise in lignin concentration post-washing (Carrillo, Staggborg, and Pineda 2014). Investigations into water-washed biomass from varied sources, including corn straw and pepper residues, corroborate substantial reductions in ash slagging (clinker formation), underscoring the method's efficacy across diverse feedstocks. Table 3 summarizes documented applications of water washing for ash-related issue mitigation.

4.2.2 Acid washing

Acid pretreatment improves ion elimination via proton (H^{+})-mediated exchange mechanisms, displacing alkali cations adsorbed on organic matrices. This process reduces boiler corrosion rates by limiting KCl/NaCl vapor deposition on superheater surfaces. Gao et al. reported barley straw treated with 7% nitric acid demonstrated >83% removal of K, Na, Ca, and Mg, alongside a 39.7% reduction in ash content (Gao et al., 2022). Subsequent thermal treatment at 230°C – 290°C under nitrogen flow (200 mL/min, 30 min) elevated the C/O ratio and improved the higher heating value. Additionally, acid pretreatment enriched bio-oil sugar concentrations by suppressing amino acid and inorganic mineral

retention. Feng et al. subjected lignocellulosic biomass (white pine, spruce, and birch bark) to 0.5 mol/L HNO_3 for 8 h (solid-liquid ratio 1:20 g/mL, ambient temperature), achieving significant potassium removal across all samples, with notable calcium reduction in spruce and birch bark (Feng et al., 2014). Comparative analyses of acids such as HCl and CH_3COOH reveal discrepancies in alkali metal extraction efficiency, ash agglomeration tendencies, and fusion temperature modulation. Representative applications of acid washing in mitigating ash-related challenges are summarized in Table 4.

While acid leaching represents a low-waste, practical approach for extracting alkali and alkaline earth metals (AAEMs) from biomass that improves ash removal efficacy and economic feasibility, its scalability is hindered by corrosive equipment degradation, residual acid accumulation risks, and environmental hazards (e.g., aquatic or terrestrial ecosystem contamination). Current research focuses on mitigating these limitations through innovations in pretreatment protocols and bio-oil refinement technologies, which are expected to enhance both sustainability and industrial applicability.

4.3 Additive

Additives are extensively employed to mitigate ash-related issues by modulating ash fusion characteristics—transforming low-melting components into thermally stable phases to increase ash fusion temperatures. These additives are classified into three primary categories: aluminosilicates, sulfur-containing compounds, and phosphorus derivatives (Wang et al., 2022). Through compositional modification of ash, additives regulate its melting behavior (Miguez et al., 2021). Li et al. demonstrated that blending sludge with biomass facilitates the formation of high-melting-point compounds such as potassium aluminosilicates (e.g., KAlSi_2O_6 and KAlSi_2O_8) and alkali phosphates [e.g., $\text{Ca}_9\text{MgK}(\text{PO}_4)_7$], enabling both resource recovery from sludge and suppression of corrosive potassium chloride emissions (Li et al., 2013). Experimental evidence indicates that $\text{Ca}_3(\text{PO}_4)_2$ not only dilutes ash constituents but also reacts with potassium salts to yield refractory phases like $\text{Ca}_{10}\text{K}(\text{PO}_4)_7$ and $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$, thereby elevating ash melting temperatures. These findings illustrate $\text{Ca}_3(\text{PO}_4)_2$'s efficacy in preventing ash sintering and fusion during biomass combustion.

Miccio et al. conducted systematic evaluations of fireclay and quartzite additives for olive pomace combustion, revealing fireclay's sustained inhibition of bed agglomeration under prolonged thermal exposure (Miccio et al., 2019). Batir et al. elucidated the potassium immobilization mechanism of kaolin: interfacial reactions between kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) and KCl/KOH generate kalsilite (KAlSiO_4), a high-melting phase that mitigates slag formation induced by alkali migration during biomass thermochemical conversion (Batir, Selcuk, and Kulah 2019). Recent studies have validated kaolin's efficacy in ash modification, particularly its unparalleled capacity for potassium chloride retention (Waqas et al., 2023). The mechanism involves thermal activation between 450°C and 600°C , where kaolinite undergoes dehydroxylation to produce reactive amorphous metakaolin ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) with concurrent release of structural water. Activated metakaolin subsequently engages in solid-state reactions with potassium species in ash,

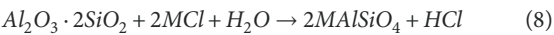
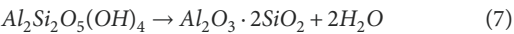
TABLE 3 Water washing as remedy to ash related problems.

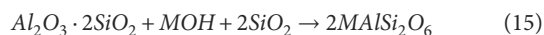
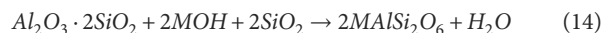
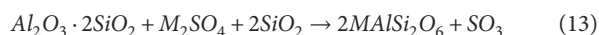
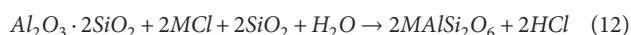
Biomass	Washing Agent	Major finding	Ref.
Wood-pellet	water	(1) hot water leaching (85°C–95°C) pretreatment of wood pellets markedly elevates the initial ash deformation temperature (IDT from 820°C to 1,400°C) (2) achieving potassium and sodium removal efficiencies of 50%–90% and 10%–90%	Gudka et al. (2016)
Sorghum	water	Reduces ash content by 20% and enhances lignin concentration by 53%	Carrillo, Staggenborg, and Pineda (2014)
Corn straw	Water	(1) H/C enrichment coupled with N/S removal was observed, while volatile matter increased to 80.31 wt% (water) (2) Ash content decreased from 8.77 wt% to 2.56 wt%	Guo et al. (2020)
Pepper	Water	(1) Hot water washing at 80°C effectively treated greenhouse crop residues, achieving 46% ash removal and significant reduction of slagging-prone inorganics (Cl, Na, Al, Fe, Si) (2) The pretreatment elevated higher calorific value by 7% and ash melting temperature to 1,200°C, as confirmed by DSC analysis, while mitigating slagging/deposition risks through optimized combustion indices	Ianez-Rodriguez et al. (2020)

TABLE 4 Acid washing as remedy to ash related problems.

Biomass	Washing Agent	Major finding	Ref.
Barley straw	HNO ₃	(1) Acid pretreatment also increased bio-oil sugar content by reducing amino acids and mineral content. Achieving >83% removal of K, Na, Ca, Mg and 39.7% ash reduction (2) Subsequent drying at 230°C–290°C under N ₂ (200 mL/min, 30 min) enhanced the C/O ratio and higher heating value	Gao et al. (2022)
White pine, white spruce, and birch bark	HNO ₃	The acid leaching effectively removed potassium across all samples, with additional calcium reduction observed in spruce and birch bark	Feng et al. (2014)
Ulva lactuca (UL) and Hydrilla verticillata (HV)	HCl	(1) Acid washing removed >96% alkaline earth metal oxides (Ca, Mg) in UL and >78% in HV (2) High sulfur in UL (27.17 wt% as SO ₃) aggravated slagging via sulfate formation. Post-acid washing, CaO content decreased from 5.43 wt% to 2.4 wt%, reducing Ca ²⁺ -SO ₄ ²⁻ fixation and enhancing sulfur volatilization	Mu et al. (2022)
Spruce bark	CH ₃ COOH	(1) 0.1 mol/mL acetic acid pretreatment achieves superior removal of Na, Cl, Ca, K, Mg (2) acid washing reduces low-melting phases (e.g., KCl, K ₂ SO ₄) by >70%, elevating slag formation temperature and mitigating ash-related fouling during thermochemical conversion	Singhal et al. (2023)

forming potassium aluminosilicate phases with melting points exceeding 1,300°C, as outlined in Equations 7–15 (Niu, Tan, and Hui 2016; Wang Xuebin et al., 2012):





5 Conclusion and prospect

5.1 Conclusion

This comprehensive review elucidates the intricate interplay between biomass ash chemistry and operational challenges in combustion systems, with a focus on slagging and corrosion mechanisms. Key findings reveal that alkali metals (K, Na), chlorine, and sulfur govern ash deposition dynamics through distinct pathways contingent on feedstock composition. High-chlorine agricultural residues exhibit KCl volatilization-condensation as the dominant slagging pathway, whereas lignocellulosic biomass is prone to sulfate-driven ash fusion. Thermodynamic analyses confirm that alkali silicate eutectics (e.g., $K_2O \cdot nSiO_2$) and chloride-induced oxide layer degradation synergistically exacerbate bed agglomeration and metallic corrosion. Mitigation strategies demonstrate that aluminosilicate additives, particularly kaolin, outperform conventional leaching pretreatments by elevating ash fusion temperatures beyond 1,300°C through interfacial reactions forming refractory kalsilite ($KAlSi_4O_8$). Hybrid approaches integrating fuel-specific preprocessing (e.g., acid washing) with optimized additive formulations achieve synergistic reductions in ash adhesion and alkali mobility, enhancing combustion efficiency. However, scalability remains constrained by unresolved challenges in fuel-additive compatibility, additive stability under thermal cycling, and residual acid contamination risks.

5.2 Prospects

Future research should prioritize three domains to advance biomass combustion technology. First, mechanistic studies on additive-ash interactions under transient thermal conditions are critical to optimize kaolin's performance while addressing its long-term stability limitations. Second, the development of bio-compatible additives-such as phosphorus-enriched mineral composites-could mitigate corrosion risks without compromising ash fusion thresholds. Third, advanced computational models coupling ash chemistry with reactor hydrodynamics are essential to predict slagging propensity across diverse feedstocks.

The authors advocate for a paradigm shift toward circular bioeconomy frameworks, emphasizing co-combustion with phosphorus-rich waste streams (e.g., sewage sludge) to valorize underutilized resources while suppressing alkali volatilization. Conversely, overreliance on acid leaching-despite its efficacy

in AAEM removal-should be cautiously evaluated due to its environmental footprint and operational complexity. Innovations in situmonitoring systems (e.g., AI-driven deposit sensors) and corrosion-resistant alloys (e.g., Cr-Mo-Ni composites) are urgently needed to bridge the gap between laboratory-scale breakthroughs and industrial deployment. Ultimately, interdisciplinary collaboration among material scientists, combustion engineers, and policymakers will be indispensable to realize biomass energy's full potential within global decarbonization agendas.

Author contributions

JL: Project administration, Supervision, Writing – original draft, Writing – review and editing. QW: Data curation, Visualization, Writing – original draft, Writing – review and editing. DS: Resources, Supervision, Writing – original draft, Writing – review and editing. BC: Visualization, Writing – original draft. PH: Conceptualization, Funding acquisition, Project administration, Resources, Supervision, Writing – original draft, Writing – review and editing. QH: Conceptualization, Funding acquisition, Project administration, Resources, Supervision, Writing – original draft, Writing – review and editing.

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Conflict of interest

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