

Release and Migration Characteristics of Potassium During Biomass Pyrolysis and Combustion (Postprint)

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Abstract

During the thermal conversion of biomass, a portion of K enters the gas phase, which can cause severe problems such as ash deposition, slagging, and high-temperature corrosion on high-temperature convective heating surfaces. This study utilizes a fixed-bed experimental system to investigate the release and migration characteristics of alkali metals during biomass pyrolysis and combustion. Experimental results indicate that: elevated temperature facilitates the release of K from wheat straw, while an oxidative atmosphere promotes K release; the pyrolysis release curves of wheat straw and rice husk differ significantly, with fuel type playing a decisive role in K release; and within the temperature range studied, the release of water-soluble K predominates.

Full Text

Preamble

Study on Release and Transformation of Potassium during Pyrolysis and Combustion of Biomass

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Abstract: During the thermal conversion process of biomass, a fraction of K can release to the gas phase, causing serious problems of deposition and corrosion on high temperature convective heating surfaces. The release and transformation of K during pyrolysis and combustion of biomass was studied in a fixed-bed experimental system. The experimental results show that an increase in the temperature is beneficial to the release of K in wheat straw, which will be facilitated in oxidizing atmosphere. There are great differences

in the release of K during pyrolysis between wheat straw and rice husk, which indicates that the fuel type plays a crucial role in the release of K. The release of water soluble K is dominant within the temperature range in this study.

Keywords: biomass; alkali metals; release characteristic; pyrolysis; combustion

0 Introduction

With growing concerns over energy and environmental issues, biomass energy has attracted increasing attention. However, biomass contains substantial alkali metals that can cause severe ash deposition, slagging, and high-temperature corrosion on boiler convective heating surfaces during pyrolysis, combustion, and gasification, representing a major obstacle to biomass energy utilization.

Previous studies have shown that both temperature and reaction atmosphere influence K release during biomass thermal conversion. Jensen et al. [2] found that K release from wheat straw was negligible below 700 °C but increased significantly at higher temperatures. Okuno et al. [3] observed a similar temperature-dependent increase in K release during pyrolysis of pine sawdust, and combustion experiments have demonstrated comparable trends [4,5]. Zhang et al. [6] investigated K release from rice straw during pyrolysis and combustion, finding that oxidizing atmospheres promote K release. Tchoffor et al. [7] further reported that gasification enhances K release from wheat straw particles compared to pyrolysis.

Inorganic constituents in biomass also affect K release. Chlorine has been shown to facilitate K release [5,8]. Dayton et al. [8] directly measured K release during switchgrass combustion using mass spectrometry, finding that KCl was the dominant gaseous K species, consistent with thermodynamic equilibrium predictions [9]. Knudsen et al. [5] observed significantly enhanced K release when dilute hydrochloric acid was added to wheat straw during combustion experiments. The release patterns of K and Cl vary with biomass type [10]. Both Knudsen et al. [5] and Zhang et al. [6] found that Si inhibits K release by forming insoluble silicate compounds during combustion, while Ca can mitigate this inhibitory effect. Deng et al. [11,12,13] demonstrated that water washing effectively removes K, S, and Cl from various biomass fuels.

As the initial stage of thermal conversion, pyrolysis profoundly influences subsequent combustion or gasification processes, making it essential to study alkali metal release during biomass pyrolysis. This study selected wheat straw and rice husk from the suburbs of Xi'an, Shaanxi Province as research subjects. Samples were crushed and sieved to obtain particles in the 150–250 μm size range. Compared with conventional fossil fuels, biomass exhibits higher volatile matter content (facilitating ignition), higher oxygen content, lower heating values (similar to lignite), and elevated alkali metal content (causing ash deposition and slagging problems). Using a fixed-bed experimental system, this work investi-

gates the effects of reaction temperature, atmosphere, and fuel type on alkali metal K release characteristics.

1.2 Experimental System

The fixed-bed experimental system for biomass thermal conversion is illustrated in [Figure 1: see original paper]. Electric heating provides the required reaction temperature. The reactor assembly consists of a quartz cup (inner diameter 25 mm), a quartz cup holder, and a quartz outer tube with side arms. The quartz cup bottom features a perforated plate to allow gas flow, covered with a high-temperature quartz filter membrane (Staplex, average pore size 0.1 μm) to prevent fuel leakage. Both ends of the quartz outer tube are sealed with silicone stoppers.

1.3 Sample Preparation

For pyrolysis experiments, $2 \pm 0.02 \text{ g}$ of biomass fuel was placed in the quartz cup, which was then positioned in the water-cooled jacket zone. A side stream of nitrogen was introduced to purge the reactor until an inert atmosphere was established. 1% of nitrogen was fed from the top, the quartz cup was pushed to the reaction zone, and pyrolysis was conducted for 30 minutes. After reaction, the cup was retracted to the water-cooled zone for cooling.

Combustion experiments followed similar procedures, except that the purge step was omitted and a synthetic gas mixture of 21% O_2 and 79% N_2 was used as the reaction gas at a flow rate of 0.5 L min^{-1} .

[Figure 2: see original paper] shows the relationship between mass loss (ωL) and reaction temperature for wheat straw and rice husk under different thermal conversion processes. Mass loss increased significantly for both fuels as pyrolysis temperature rose from $400 \text{ }^\circ\text{C}$ to $1000 \text{ }^\circ\text{C}$. Under combustion conditions, mass loss exceeded 95% for wheat straw due to its low ash content, showing limited variation.

1.4 Analytical Methods

To investigate the effects of reaction atmosphere and fuel type on K release characteristics, total K content in char and ash samples from wheat straw and rice husk was measured at various temperatures. Samples were first digested, diluted, and filtered before analysis using ICP-OES (Perkin Elmer, USA).

To analyze the relationship between different K occurrence forms in wheat straw char, chemical fractionation was performed using the method proposed by Baxter et al. [14], categorizing K into four forms: (1) water-soluble K compounds, (2) ion-exchangeable K compounds soluble in ammonium acetate solution, (3) acid-soluble K salts soluble in hydrochloric acid, and (4) insoluble K-containing residues.

2.1 Effects of Reaction Temperature and Atmosphere on K Release

Pyrolysis and combustion experiments with wheat straw were conducted at 400–1000 °C, with results shown in [Figure 3: see original paper]. During pyrolysis, K release rates ($\omega_R(K)$) were low ($<5\%$) at 400–500 °C, but increased continuously with temperature, reaching 40.8% at 1000 °C. In combustion experiments, K release showed a notable increase when temperature rose from 700 °C to 800 °C, attaining 49.3% at 1000 °C.

Although K release rates were higher in combustion than in pyrolysis, the difference was modest. At 800 °C, combustion promoted approximately 8.7% additional K release compared to pyrolysis, and about 8.5% more at 1000 °C. These results demonstrate that oxidizing atmospheres facilitate gaseous K release from wheat straw particles, though temperature exerts a more significant influence under the experimental conditions investigated.

2.2 Effect of Fuel Type on K Release

Pyrolysis experiments were performed on wheat straw and rice husk of the same particle size range at 400–1000 °C. By measuring total K content in the resulting char samples, the relationship between K release rate and pyrolysis temperature was obtained, as shown in [Figure 4: see original paper].

The release curves for the two biomass types show similar trends but differ substantially in detail. For wheat straw, K release was minimal at 400–500 °C, increased sharply at 600 °C (attributed to decomposition of organic K, as the vapor pressure of K-containing inorganic salts is low [15,16,17]), and continued to rise significantly above 700 °C. Literature indicates that HCl and tar-associated Cl are completely released at low temperatures [18]; therefore, the incremental K release above 700 °C likely occurs through volatilization with Cl as KCl. Overall, K release from wheat straw occurs in two stages: decomposition of organic K and subsequent volatilization of KCl. In contrast, K release from rice husk increased steadily with temperature, stabilizing at approximately 0.45 mg g⁻¹, likely due to inhibition by its inherent high Si content forming silicates [5,6]. These findings indicate that fuel type plays a decisive role in K release behavior.

2.3 Effects of Reaction Temperature and Atmosphere on K Transformation

To investigate K transformation characteristics, chemical fractionation was performed on wheat straw char and ash samples prepared at different reaction temperatures. The mass fractions ($\omega(K)$) of various K occurrence forms are presented in [Figure 5: see original paper]. In both pyrolysis and combustion, water-soluble K constitutes the main released fraction, while the proportion of insoluble K increases with temperature.

As shown in [FIGURE:5(a)], during wheat straw pyrolysis at 600–900 °C, the combined amount of ion-exchangeable K, acid-soluble K, and insoluble K remained essentially constant, though their relative proportions changed. This suggests that some ion-exchangeable K converted to acid-soluble K, with an even greater portion transforming into insoluble K. [FIGURE:5(b)] reveals that under combustion conditions, increasing temperature caused water-soluble K to partially volatilize to the gas phase while another portion underwent solid-phase transformation. Together with originally present ion-exchangeable K and acid-soluble K, this fraction ultimately converted to insoluble K retained in the solid phase.

Fuel type determines not only the total alkali metal content but also the distribution of K occurrence forms. Water-soluble K dominates the release process and largely characterizes the K release potential, whereas insoluble K exists in a strongly bound, inert state and represents an important form of K retention in the solid phase.

2.4 Interaction Between Different Fuels Under Pyrolysis Conditions

To investigate interactions between different fuels, co-pyrolysis experiments were conducted on wheat straw and rice husk mixtures of the same particle size range at 700–1000 °C. By measuring total K content in the resulting char, the relationship between K release rate and rice husk blending ratio (ϕ_{RH}) was obtained, as shown in [Figure 6: see original paper]. The dotted lines in the figure represent ideal release amounts obtained by direct connection of individual fuel release values at corresponding temperatures, indicating the expected release without fuel interaction. All release amounts have been normalized to per unit mass of fuel.

At 700–900 °C, the measured release from mixed samples fell essentially on the dotted lines, suggesting negligible interaction between the two fuels regarding alkali metal release. This may be attributed to the char structure hindering reactions between K and Si, thereby affecting silicate formation [2]. At 1000 °C, however, K release was significantly reduced, decreasing by approximately 0.76 mg g⁻¹ at a 70% rice husk blending ratio. This indicates that high temperatures can disrupt the char structure, promoting silicate formation and inhibiting K release.

Conclusions

This study employed a fixed-bed experimental system to investigate the effects of reaction temperature, atmosphere, and fuel type on alkali metal migration characteristics. The results show that:

- (1) Elevated temperature promotes K release, while oxidizing atmospheres facilitate gaseous K release from wheat straw particles.

- (2) The distinct pyrolysis release curves of wheat straw and rice husk demonstrate that fuel type plays a decisive role in K release behavior.
- (3) For different occurrence forms of K in wheat straw, during pyrolysis at 600–900 °C, some ion-exchangeable K converts to acid-soluble K, with an even greater portion transforming into insoluble K. Under combustion conditions at 1000 °C, 12.56% of K converts to insoluble K retained in the solid phase. Within the temperature range investigated, water-soluble K release dominates the process.
- (4) Co-pyrolysis of wheat straw and rice husk at 1000 °C reduces K release, with a decrease of approximately 0.76 mg g⁻¹ at a 70% rice husk blending ratio.

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