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

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Abstract

During biomass thermal conversion, a portion of K enters the gas phase, causing serious problems such as ash deposition and slagging on high-temperature convective heating surfaces and high-temperature corrosion. 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 oxidizing 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; within the temperature range studied, the release of water-soluble K is dominant.

Full Text

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

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Abstract

During the thermal conversion of biomass, a portion of potassium (K) is released into the gas phase, causing severe problems such as ash deposition, slagging, and high-temperature corrosion on convective heating surfaces. This study investigates the release and transformation characteristics of K during biomass pyrolysis and combustion using a fixed-bed experimental system. The results demonstrate that increasing temperature enhances K release from wheat straw, with this effect being further promoted under oxidizing atmospheres. Significant differences in K release profiles were observed between wheat straw and rice husk, indicating that fuel type plays a decisive role in K release behavior. Within the temperature range investigated, the release of water-soluble K was found to be dominant.

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, the high alkali metal content in biomass leads to 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 affect K release during biomass thermal conversion. Jensen et al. [2] found that K release from wheat straw during pyrolysis 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. Comparable trends have been reported in combustion experiments [4,5]. Zhang et al. [6] investigated K release from rice straw during pyrolysis and combustion, finding that oxidizing atmospheres promoted K release. Tchoffor et al. [7] reported that gasification enhanced K release from wheat straw particles compared to pyrolysis.

Inorganic components in biomass also influence K release. Previous research [5,8] has shown that chlorine (Cl) facilitates K release. Dayton et al. [8] directly measured K release during switchgrass combustion using mass spectrometry, finding that K existed primarily as KCl in the gas phase, 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. The release patterns of K and Cl vary with biomass type [10]. 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 types.

As the initial stage of thermal conversion, pyrolysis profoundly influences subsequent combustion or gasification processes, making it crucial to investigate alkali metal release during biomass pyrolysis. This study examines wheat straw and rice husk collected from the suburbs of Xi’ an, Shaanxi Province. Samples were crushed and sieved to obtain particles in the 150–250 m size range. Compared to conventional fossil fuels, biomass exhibits higher volatile matter content (facilitating ignition), higher oxygen content, lower heating values (similar to lignite), and higher alkali metal content (causing slagging and deposition issues).

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1 Experimental

1.1 Fuel Characterization

Wheat straw and rice husk were selected as feedstocks. After crushing, particles in the 150–250 m range were used for experiments. Biomass fuels contain higher volatile matter than conventional fossil fuels, making them easier to ignite. They also have higher oxygen content and lower heating values (comparable to lignite), along with elevated alkali metal levels that can cause slagging and deposition problems.

1.2 Experimental System

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

1.3 Sample Preparation

For pyrolysis experiments, 2±0.02 g of biomass fuel was placed in the quartz cup, which was then positioned in the water-cooled zone. A side stream of nitrogen was introduced for purging until an inert atmosphere was established. A nitrogen flow of 0.5 L min ^{1} was then introduced from the top, the quartz cup was pushed to the reaction zone, and pyrolysis was conducted for 30 min. After reaction, the cup was retracted to the water-cooled zone for cooling.

Combustion experiments followed similar procedures, but without the purging step, using a synthetic gas mixture of 21% O and 79% N at 0.5 L min ^{1} as the reaction gas.

[Figure 1: see original paper] shows the schematic of the fixed-bed experimental system.

[Figure 2: see original paper] presents the mass loss (L) of wheat straw and rice husk under different thermal conversion processes as a function of reaction temperature. Mass loss increased significantly for both fuels as pyrolysis temperature rose from 400 °C to 1000 °C. Under combustion conditions, mass loss exceeded 95% for wheat straw due to its low ash content, showing limited variation.

1.4 Analysis Methods

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

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

2 Results and Discussion

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 (R(K)) was low (<5%) at 400–500 °C, but increased continuously with temperature, reaching 40.8% at 1000 °C. In combustion experiments, K release increased when temperature rose from 700 °C to 800 °C, reaching 49.3% at 1000 °C.

Compared to pyrolysis, combustion yielded higher K release rates, though the difference was modest. At 800 °C, combustion promoted approximately 8.7% additional K release, and at 1000 °C, about 8.5% more. These results indicate that oxidizing atmospheres facilitate gaseous K release from wheat straw particles, though temperature exerts a more pronounced effect 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 the total K content in char samples, the relationship between K release rate and pyrolysis temperature was obtained, as shown in [Figure 4: see original paper].

Both biomass types exhibited similar trends in release profiles, but with significant differences 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 inorganic K salts is low [15,16,17]), and continued to rise substantially above 700 °C. Literature indicates that HCl and tar-associated Cl are completely released at low temperatures [18]; thus, the incremental K release above 700 °C likely results from co-release with Cl as KCl. Overall, K release from wheat straw occurs in two stages: decomposition of organic K and volatilization of KCl. In contrast, K release from rice husk increased steadily with temperature, plateauing around 0.45 mg g ^{1}, likely due to inhibition by inherent silica [5,6]. These results demonstrate 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 char and ash samples from wheat straw at different reaction temperatures. The mass fractions ((K)) of various K species are shown in [Figure 5: see original paper]. Water-soluble K dominated K release in both pyrolysis and combustion, with the proportion of insoluble K increasing with temperature.

As shown in [FIGURE:5(a)], during wheat straw pyrolysis at 600–900 °C, the combined amount of ion-exchangeable K, HCl-soluble K, and insoluble K remained relatively constant, though their proportions changed. This suggests that some ion-exchangeable K transformed into HCl-soluble K, with an even greater portion converting to insoluble K. [FIGURE:5(b)] reveals that under combustion conditions, increasing temperature caused water-soluble K to either release to the gas phase or transform in the solid phase, with ion-exchangeable K and acid-soluble K ultimately converting to insoluble K that remained in the solid phase.

Fuel type determines not only the total alkali metal content but also the distribution of K species. Water-soluble K dominates K release and largely determines the release potential, whereas insoluble K is strongly bound and inert, representing the primary form of K retained in the solid phase.

2.4 Interactions Between Different Fuels During Pyrolysis

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

At 700–900 °C, the measured release from mixed fuels fell nearly on the dotted lines, suggesting minimal interaction between the two fuels regarding K release. This may be because the char structure hindered reactions between K and Si, affecting silicate formation [2]. At 1000 °C, however, K release was significantly suppressed, 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.

3 Conclusions

This study investigated the effects of reaction temperature, atmosphere, and fuel type on alkali metal migration characteristics using a fixed-bed experimental system. The main findings are:

1. Increasing temperature promotes K release, while oxidizing atmospheres facilitate gaseous K release from wheat straw particles.
2. Significant differences in K release profiles between wheat straw and rice husk demonstrate that fuel type plays a decisive role in K release behavior.
3. For different K species in wheat straw, during pyrolysis at 600-900 °C, some ion-exchangeable K transforms into HCl-soluble K, with an even greater portion converting to insoluble K. Under combustion conditions at 1000 °C, 12.56% of K is converted to insoluble K retained in the solid phase. Within the investigated temperature range, water-soluble K release dominates.
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.

References

[1] Scott Q T, Charles M K, Darren M I. Removal of Inorganic Constituents of Biomass Feedstocks by Mechanical Dewatering and Leaching[J]. Biomass and Bioenergy, 1997, 12(4):241-252.

[2] Jensen P A, Frandsen F J, Dam J K, et al. Experimental Investigation of the Transformation and Release to Gas Phase of Potassium and Chlorine during Straw Pyrolysis[J]. Energy Fuels 2000, 14, 1280—1285.

[3] Okuno T, Sonoyama N, Hayashi J, et al. Primary Release of Alkali and Alkaline Earth Metallic Species during the Pyrolysis of Pulverized Biomass[J]. Energy Fuels 2005, 19, 2164—2171.

[4] Lith S C V, Jensen P A, Frandsen F J, et al. Release to the Gas Phase of Inorganic Elements during Wood Combustion. Part 2: Influence of Fuel Composition[J]. Energy & Fuels, 2008, 22(3):1598-1609.

[5] Knudsen J N, And P A J, Damjohansen K. Transformation and Release to the Gas Phase of Cl, K, and S during Combustion of Annual Biomass[J]. Energy & Fuels, 2004, 18(5):págs. 1385-1399.

[6] ZHANG Zhihao, SONG Qiang, YAO Qiang, et al. Influence of the Atmosphere on the Transformation of Alkali and Alkaline Earth Metallic Species during Rice Straw Thermal Conversion[J]. Energy Fuels, 2012, 26(3):1892-1899.

[7] Tchoffor P A, Davidsson K O, Thunman H. Effects of Steam on the Release of Potassium, Chlorine, and Sulfur during Char Conversion, Investigated under Dual-Fluidized-Bed Gasification Conditions[J]. Energy & Fuels, 2014, 28(11):6953-6965.

[8] Dayton D C, French R J, Milne T A. Direct Observation of Alkali Vapor Release during Biomass Combustion and Gasification. 1. Application of Molecular Beam/Mass Spectrometry Switchgrass Combustion[J]. Energy & Fuels, 1995, 9(5):855-865.

[9] WEI Xiaolin, Schnell U, Hein K R G, et al. Behaviour of Gaseous Chlorine and Alkali Metals during Biomass Thermal Utilisation[J]. Fuel, 2005, 84(7-8):841-848.

[10] Keown D M, Favas G, Hayashi J, et al. Volatilisation of Alkali and Alkaline Earth Metallic Species during the Pyrolysis of Biomass: Differences between Sugar Cane Bagasse and Cane Trash[J]. Bioresource Technology, 2005, 96(14):1570-7.

[11] DENG Lei, ZHANG Tao, CHE Defu. Effect of Water Washing on Fuel Properties, Pyrolysis and Combustion Characteristics, and Ash Fusibility of Biomass[J]. Fuel Processing Technology, 2013, 106(106):712-720.

[12] DENG Lei, CHE Defu. Chemical, Electrochemical and Spectral Characterization of Water Leachates from Biomass[J]. Industrial & Engineering Chemistry Research, 2012, 51(48):15710-15719.

[13] 邓磊, 张涛, 刘银河, 等. 水洗对生物质燃料特性及燃烧特性的影响 [J]. 工程热物理学报, 2010, 31(7):1239-1242. DENG Lei, ZHANG Tao, LIU Yinhe, et al. Effect of Washing on Fuel Properties and Combustion Characteristics of Biomass[J]. Journal of Engineering Thermophysics, 2010, 31(7):1239-1242.

[14] Jenkins B M, Baxter L L, Miles T R, et al. Combustion Properties of Biomass[J]. Fuel Processing Technology, 1998, 54(1-3):17-46.

[15] Dayton D C, Jenkins B M, Turn S Q, et al. Release of Inorganic Constituents from Leached Biomass during Thermal Conversion[J]. Energy Fuels 1999, 13, 860−870.

[16] Kowalski T, Ludwig C, Wokaun A. Qualitative Evaluation of Alkali Release during the Pyrolysis of Biomass[J]. Energy Fuels 2007, 21, 3017−3022.

[17] Quyn D M, Wu H, Bhattacharya S P, et al. Volatilisation and Catalytic Effects of Alkali and Alkaline Earth Metallic Species during the Pyrolysis and Gasification of Victorian Brown Coal. Part II. Effects of Chemical Form and Valence[J]. Fuel 2002, 81, 151−158.

[18] ZHAO Haibo, SONG Qiang, WU Xingyuan, et al. Study on the Transformation of Inherent Potassium during the Fast-Pyrolysis Process of Rice Straw[J]. Energy Fuels, 2015, 29, 6404-6411.

Note: Figure translations are in progress. See original paper for figures.