

Release and Transformation of Potassium during Gasification of Biomass

Guangcai Zhang¹, Shihao Ma², Yikun Wang¹, Yuan Tie², Lei Deng^{2*}, Defu Che²

¹ Xi'an Thermal Power Research Institute Co., LTD., Xi'an 710054, China

² State Key Laboratory of Multiphase Flow in Power Engineering, School of Energy and Power Engineering, Xi'an Jiaotong University, Xi'an 710049, China (leideng@mail.xjtu.edu.cn)

ABSTRACT

To investigate the release and transformation of fuel potassium during biomass gasification, paulownia wood is used in a fixed-bed reactor system during 500–900 °C. Chemical fractionation analysis are performed to study the existing form of fuel potassium. The influences of particle size and gasification temperature are discussed. The results show that release ratio of potassium increases with the gasification temperature. When the temperature is higher than 700 °C, the content of water-soluble and NH₄Ac-soluble K decreases, and part of other occurrence modes of K turn into the insoluble K gradually. The release ratio of potassium with three different particle sizes reaches 26.65%, 32.53% and 40.56% respectively at 900 °C. Increase of particle size inhibits the potassium release and induces the formation of NH₄Ac-soluble K. For centimeter-sized samples, potassium content at central is higher than that of surface at 700 °C, which is related to the formation of NH₄Ac-soluble potassium. The content of potassium at different positions decreases significantly above 700 °C.

Keywords: potassium release, transformation, biomass gasification

1. INTRODUCTION

With the fossil energy crisis and the requirements of environmental protection, the use of renewable energy has become an inevitable choice. As the only carbon-based renewable energy source, biomass has attracted extensive attention due to its renewable and carbon-neutral characteristics [1, 2]. However, biomass contains a large amount of alkali metals and alkaline earth metal elements (AAEMs), which will be released into the gas phase during the thermal conversion, causing problems such as fouling, slagging and high temperature corrosion of heat exchange equipment [3,

4]. On the other hand, the AAEMs remained in the solid phase have a catalytic effect on the thermal conversion of biomass. Therefore, it is of great significance to study the release and transformation of potassium.

At present, the research on AAEMs migration in biomass transformation mainly focuses on pyrolysis and combustion. These results show that the increase of temperature promotes the release of AAEMs in biomass. In addition, the release of potassium is also associated with the other content in biomass. It is well demonstrated that a relatively high Cl content would promote potassium release in the form of KCl [5]. While, a relatively high Si content could reduce the volatility of potassium by bounding potassium to alminosilicates [6] or incorporating potassium into silicate networks. However, only limited attention has been focused on the transformation of occurrence mode of fuel potassium during biomass CO₂ gasification. Due to the high cost of biomass puerized process, it is of significance to study the release and transformation of potassium during biomass gasification with large particles.

In this study, biomass gasification experiments are performed in a fixed-bed reactor system. The influence of biomass particle and gasification temperature has been discussed in detail. The release of fuel potassium is determined quantitatively based on mass balance during CO₂ gasification. The transformation of potassium occurrence mode in raw sample and residue is examined at different temperatures through chemical fractionation analysis. In addition, different positions of the sample are sampled and the law of potassium precipitation in space is analyzed.

2. MATERIALS AND METHODS

2.1 Sample Preparation

The experiment uses paulownia wood as raw material, which collected from Shandong Province, China. In order to study the migration of potassium in the process of large-particle biomass gasification, there exists two sizes for the cylindrical biomass, namely a diameter of 18 mm and a height of 10 mm, and a diameter of 3 mm and a height of 2 mm. The paulownia wood is also pulverized and particles with a size of 100-125 μm are saved. Then, all three samples are dried at 105 $^{\circ}\text{C}$ for 10 h and sealed for experiment. The fuel properties of biomass samples are presented in Table 1 and Table 2.

Table 1. Proximate and ultimate analyses

Proximate analysis				
A_d	V_{daf}	FC_{ad}	M_{ad}	
0.43	77.26	20.87	7.82	
Ultimate analysis				
C_d	H_d	O_d	N_d	S_d
50.97	5.77	42.66	0.13	0.04

Table 2. Main ash-forming elements

K	Na	Ca	Mg	Al	Cl	Si
0.4190	0.0356	0.1410	0.0208	0.0268	0.0419	0.0614

2.2 Gasification Experiment

To simulate the conditions on the grate of the biomass-gasification boiler, a gasification experiments are performed from 500 to 900 $^{\circ}\text{C}$ in a fixed-bed reactor. As shown in Fig. 1, the reaction system consists of a gas supply system, a reaction system and an exhaust gas treatment system. Reactions occur in the quartz and the diameter of the quartz basket is slightly smaller than the diameter of the quartz reactor to ensure the basket can move up and down freely. Before experiment the quartz reactor is heated to a preset temperature and the quartz basket with biomass sample is inserted into the constant temperature zone. Reaction gases of CO_2 (750 mL min^{-1}) goes through the reactor from the top to the bottom, the duration time of biomass gasification is 20 min. At the end of the experiment, the quartz basket is withdrawn and the mass flow meter is switched from of the CO_2 to N_2 to cooling the samples. After be cooling, residual sample is collected and weighted.

2.3 Analysis

The release and transformation of potassium during biomass gasification is determined based on weight measurements and elemental analyses, and chemical fractionation analysis. The details are described in our earlier study [7]. The total potassium contents of the raw biomass samples as well as the residual samples are measured using a microwave digestion system (Multiwave 3000, Anto Paar, Austria) and an inductively coupled plasma-optical emission spectroscopy (ICP-OES, Perkin Elmer, USA). Sequential extractions are performed on the samples with deionized water, $\text{CH}_3\text{COONH}_4$ (i.e. NH_4Ac) of 1.0 mol L^{-1} , and HCl of 1.0 mol L^{-1} . Finally, the potassium contents in the solutions are measured by ICP-OES. And mass fractions of water-soluble K, NH_4Ac -soluble K (ion-exchangeable K), HCl -soluble K, and insoluble K are obtained. All the measurements are repeated three times for repeatability.

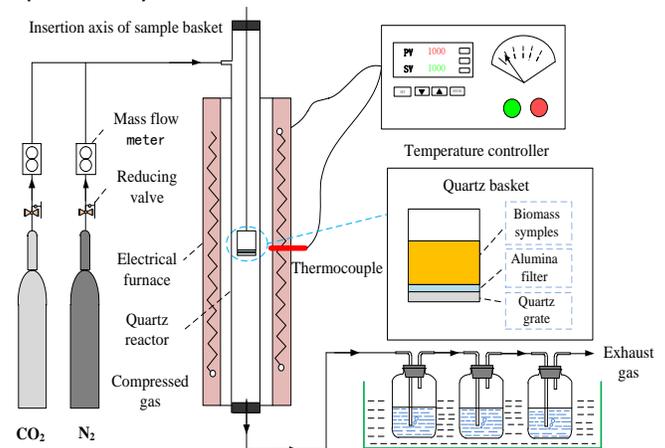


Fig. 1. The fixed-bed reactor system of biomass gasification.

3. RESULTS AND DISCUSSION

3.1 Potassium Release to the Gas Phase

Fig. 2 shows the influence of particle size on the release of potassium during gasification. When gasification temperature rises, more potassium enters the gas phase. When temperature is lower than 700 $^{\circ}\text{C}$, there exists no significant increase of potassium since part of potassium is converted to organic K and retained in biomass char. When temperature is higher than 700 $^{\circ}\text{C}$, an abrupt increase occurs. This could be caused by the decomposition of organic potassium at temperatures above 700 $^{\circ}\text{C}$. In addition, the release rate of potassium decreases with the increase of particle size. On the one hand, the large size limits the diffusion of potassium; on the other hand, a series of chemical reactions of potassium lead to the immobilization of potassium in the char.

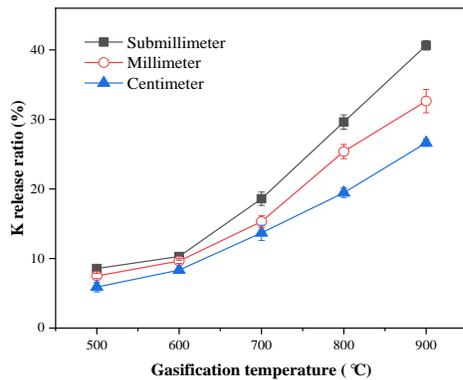


Fig. 2. K release at different gasification temperatures.

3.2 Potassium Transformation during Gasification

The potassium transformation during biomass gasification is illustrated as the distribution ratio of potassium in the gas and solid phases. The results of sub-millimeter samples are shown in Fig. 3. The water-soluble K is easier to be released compared with other occurrence modes of K. Nearly all the released K seems to be originated from the water-soluble K. A sudden increase occurs in the distribution ratio of NH_4Ac -soluble K at 600 and 700 °C. Both contents of NH_4Ac -soluble and HCl-soluble K decrease while the content of insoluble K increases at temperatures above 700 °C. It means that other occurrence modes of K except water-soluble part turn into the insoluble K gradually.

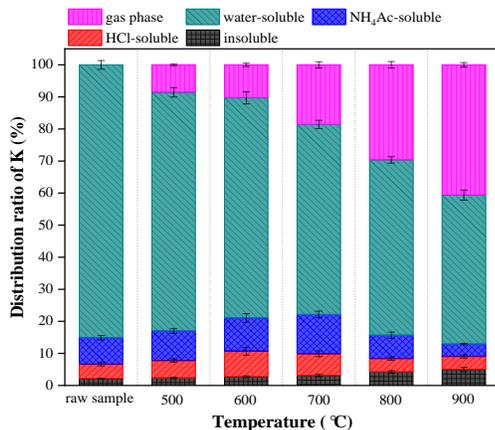


Fig. 3. K transformation for sub-millimeter sized particle samples.

As we can see from Fig. 3 and Fig. 4, there still exists difference among the distribution of K though the influence of particle size on the transformation of potassium during biomass gasification is limited. The content of organic potassium increases with the particle size. The highest content of NH_4Ac -soluble K occurs at 700 °C, owing to the decomposition of NH_4Ac -soluble K at higher temperatures.

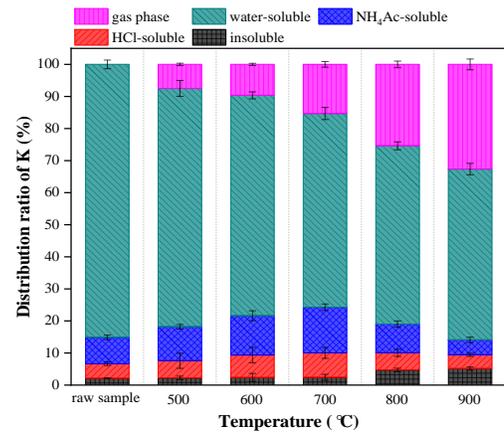


Fig. 4. K transformation for millimeter-sized particle samples.

Fig. 5 shows the K transformation of centimeter-sized samples at different gasification temperatures. Compared with the transformation of K of the other samples, the content of organic potassium of centimeter-sized samples is highest at 700 °C. Large size permits a longer residence time of volatiles precursors, which is beneficial for the formation of NH_4Ac -soluble K. Similar results had also been reported [8], and the possible reaction for this phenomenon is shown in formula (1).

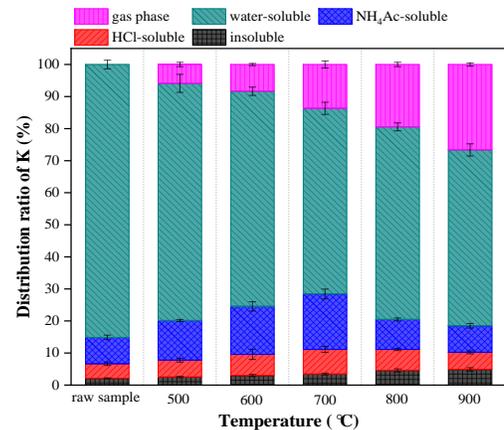
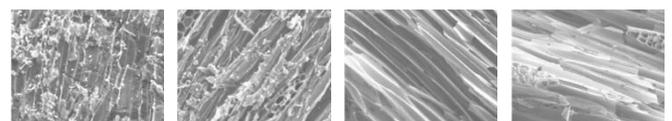
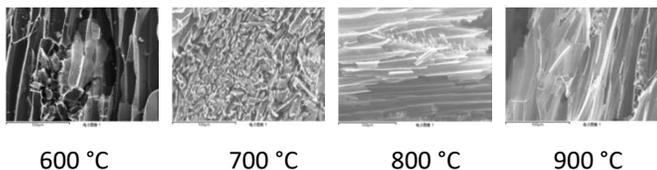


Fig. 5. K transformation for centimeter-sized particle samples.

3.3 The spatial distribution of K with centimeter-sized particle sample



(a) K content at the surface of samples



(b) K content at the center of samples

Fig. 6. SEM result of different positions of samples at different gasification temperatures.

Table 3. K Content at different positions

Temperature/°C	600	700	800	900
K content at the surface	1.56%	1.74%	0.58%	0.76%
K content at the center	0.96%	1.99%	0.6%	0.55%

In order to further study the release of K of centimeter-sized particles in spatial, SEM-EDX analysis is conducted at the surface and center of the char samples. The results are shown in Figure 6 and Table 3 respectively. With the increase of temperature from 600 to 700 °C, the contents of K at outer surface and central increase, and the increase of potassium at central is much greater than that of potassium at surface. Part of water-soluble potassium transforms to organic forms. Compared to the surface, volatile precursor has longer residence time, which is beneficial to the reaction between volatile precursor and K. The potassium content decreases significantly as the organic potassium begins to decompose at 800 °C. As the result, the difference between the internal and external potassium contents in particle size gradually decreased.

4. CONCLUSIONS

The release and transformation of fuel potassium is investigated through gasification of paulownia wood samples in a fixed-bed reactor system. The effects of particle size and gasification temperature are evaluated. The release ratio of potassium increases with the gasification temperature and there exists an abrupt increase when temperature is higher than 700 °C. When the temperature reaches 900 °C, the release ratio of K with sub-millimeter, millimeter-sized and centimeter-sized particle reaches 26.65%, 32.53% and 40.56% respectively. In addition, the K distribution in space of centimeter size particle biomass vary with different gasification temperatures. Content of K at surface is higher than that of central position at 600 and 900 °C, while the trend is the opposite at 700 and 800 °C.

ACKNOWLEDGEMENT

This work has been financially supported by Science and Technology Project of China Huaneng Group (HNKJ18-H09).

REFERENCE

- [1] Saidur, R. et al. A review on biomass as a fuel for boilers. *J Sci Commun* 2011. 15(5): p. 2262-2289.
- [2] Frandsen, F.J. Utilizing biomass and waste for power production - A decade of contributing to the understanding, interpretation and analysis of deposits and corrosion products. *J Sci Commun* 2005. 84(10): p. 1277-1294.
- [3] Simone C. van Lith, F.J.F. Melanie Montgomery, Tommy Vilhelmsen and Søren A. Jensen, Lab-scale Investigation of Deposit-induced Chlorine Corrosion of Superheater Materials under Simulated Biomass-firing Conditions. Part 1: Exposure at 560 °C. *J Sci Commun* 2009. 23: p. 3457-3468.
- [4] Miles, T.R. et al. Boiler deposits from firing biomass fuels. *J Sci Commun* 1996. 10(2): p. 125-138.
- [5] Jacob N. Knudsen, P.A.J.K.D.J. Transformation and Release to the Gas Phase of Cl, K, and S during Combustion of Annual Biomass. *J Sci Commun* 2004. 18: p. 1385-1399.
- [6] Zhao, H.B. et al. Study on the Transformation of Inherent Potassium during the Fast-Pyrolysis Process of Rice Straw. *J Sci Commun* 2015. 29(10): p. 6404-6411.
- [7] Deng, L. et al. Transformation and release of potassium during fixed-bed pyrolysis of biomass. *J Sci Commun* 2018. 91(4): p. 630-637.
- [8] Davidsson, K.O. et al. Alkali Emission from Birchwood Particles during Rapid Pyrolysis. *J Sci Commun* 2012. 16(5): p. 1033-1039.