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Experimental study on the influences of operating parameters on the retention of potassium during the biomass combustion

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Abstract

Quantify the potassium in biomass combustion residues is an alternative way to study the release mechanisms of potassium which is essential to mitigate the ash-related problems while using biomass fuels. In this work, different combustion parameters were used to study the retention of potassium via high-temperature furnace balance system and then Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). Through the investigation, final temperature influences the retention of potassium the most, there is 80% of potassium left when temperature is 200℃, while this number sharply dropped to 42% when temperature reaches 1000℃. There is a little different of the retained potassium between the heating rate of 500℃/h and 1000℃/h at selected temperatures, while the high heating rate (1500℃/h) results in the 20% less of retained potassium compared to that of the heating rate of 1000℃/h. The influence of isothermal time is insignificant when temperature <900℃, but at high temperature like 1000℃, the longer the isothermal time, the much less potassium that left.

Keywords: Biomass; Combustion; Potassium retention; Final temperature; Heating rate; Isothermal time

1. Introduction

The renewable and environmentally friendly characteristics of biomass have drawn more attention worldwide. It is believed that taking biomass as a combustion feedstock for the energy industries is a prospective approach for the utilization of biomass fuels [1]. However, the combustion of biomass fuels has proven to be a technical challenge, due to the ash related slagging and fouling problems [2, 3], which are caused by its high content of potassium, chlorine, and sulfur. Researchers have revealed that much of the organic and inorganic forms of potassium found in raw biomass are volatilized which can result in undesirable deposition and corrosion effects as the condense out on plant surfaces, and leading to ash deposition after rejoining with other solid phase ash particles [2]. Potassium is an essential nutrient for the plant growth and is presenting in much higher quantities in most solid biomass fuels (up to 1.3 wt% [4]) than traditional fossil fuels, which could cause severer corrosion

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damage to the plant. So the study of the transition mechanisms of potassium is crucial to optimize biomass combustion by enhancing the plant design.

During the biomass combustion process, the inherent potassium in biomass can either be released as gaseous or retained in the solid residues [3, 5]. Scholars have been studied the release mechanisms of potassium in gaseous phase for decades. Simon et al. [6] reported that small amount of potassium (<15%) has been released when temperature below 700℃, but large fraction of potassium will be released when temperature reaches 1000℃. The release mechanisms of potassium has also been investigated in the recent studies [7, 8]. However, there is still a lack of comprehensive investigation on the retention of potassium in the solid residues after combustion. Knowing its retention mechanisms can help us to further understand how the potassium being transferred during the combustion process, besides, it's more convenient and accurate to track and quantify the potassium in solid residues. Operating parameters play a major role to affect the composition and properties of thermal conversion of biomass [9], and important for the emission from the combustion processes [10]. During the reactions, many factors affect the extent and rate of the thermal fragmentations of the productions, like: temperature, heating rate, isothermal times and biomass feed et al [9], among which, both the final temperature and the isothermal time at the final temperature have an impact in the composition of the products [11], while the heating rate affects the reactivity in reactions during the thermal conversion of biomass [12], and these could significantly influence the release of potassium. Understanding how they affect the retention of potassium can help us to optimize the reaction process, and to control the ash problems, therefore, will have great implications for developing clean and efficient utilization technologies for biomass, thus, will prolong the service life of biomass burning plants which will make the biomass fuel more economically competitive.

Our previous study [13] has present an alternative test device which can test a large amount of biomass compared to TGA device, so the aim of this study is to use the high-temperature furnace balance system along with the ICP-OES to investigate the influence of final temperature, heating rate and isothermal time on the retention of potassium in solid residues.

2. Materials and methods

2.1. Biomass fuel

Wheat straw pellets are used in this study, which were purchased from Agripellets Ltd. Each pellet is about 4 cm in length, 0.5cm in diameter and weighted about 1 g. The pellets were air dried and stored in sealed containers before tests. The proximate and ultimate analysis of the pellets is presented in Table 1.

Table 1. Proximate and ultimate analysis of straw pellets

	Wt, %		Wt, %
M_{ad}	9.3	C_{db}	45.2
V_{db}	74.8	H_{db}	5.25
FC_{db}	17.8	O_{db}	41.2
A_{db}	7.4	N_{db}	0.71

**ad=air dry; db=dry basis*

2.2. Experimental set up

A costumer designed high-temperature furnace balance system is applied to run the tests. Previous study [13] has illustrated the accuracy and replicability of the results by using the device, the scheme of the device is showed in Fig 1. In this study, three different operating parameters are used to prepare the solid residues: final temperature, heating rate and isothermal time. 5±0.5g pellets are tested in the furnace balance system with the set of different combustion conditions, the tests scenarios are summarized below in Table 2. After the combustion tests, the residues are collect, milled into fine particles and microwave digested, then Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) is used to quantify the K concentration, in this way, the influence of the combustion parameters on the retention of K is investigated.

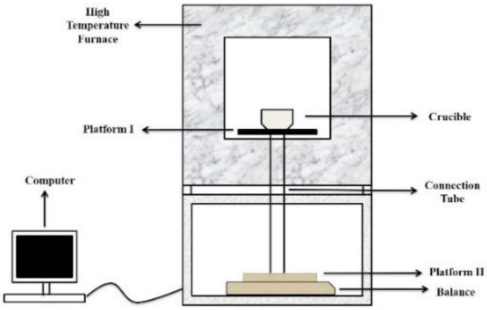

Fig.1. Schematic of the high temperature furnace balance system

Table 2. Summary of testing conditions

Operating parameters \ Test conditions	Temperature, ℃	Heating rate, ℃/h	Isothermal time, min
Final temperature	200-1000 (with 100 interval)	1000	5
Heating rate	300; 400; 600; 900; 1000	500; 1000; 1500	5
Isothermal time	300; 400; 600; 900; 1000	1000	5; 10; 20

3. Results and discussion

3.1 Influence of final temperature on the retention of potassium

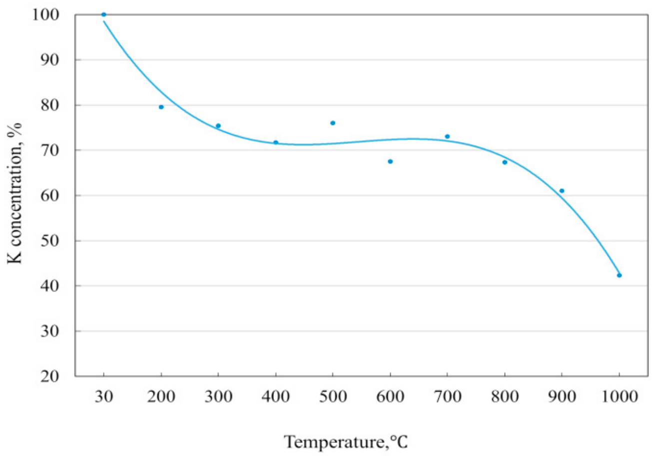

Fig 2. The change of K content (dry basis) with the change of final temperature

The results of K content in the residues under different final temperatures are shown in Fig 2, there are two notable drops can be observed from the figure. In the first drop, the loose of K content start from 200℃, and quickly dropped till temperature reaches 400℃, there is about 70% of K left in the solid residue, within this temperature range, the loss of K content is mainly caused by the release of weakly bonded K and organic K [5, 14], which are thermally unstable. The decomposed K at lower temperature is mainly in the form of K+ and then can react with H_2O and Cl to generate KOH and KCl and released [15]; After the first stage of decreasing, the K content continues to drop mildly till 700℃, the variation of retained K under each temperature is small, and 5% more K has been lost during this temperature range, due to the oxidation and decomposition of char-K; When temperature exceeds 700℃, the second drop of K content occurred, and there is only 42% of K left when temperature reaches 1000℃, the substantially decrease of K content is caused by the release of KOH/KCl, as well as the decomposition of inorganic K such as: K_2CO_3 [16] and the evaporation of K_2SO_4 [6].

It can be seen that before 700℃, the lost K content is small, and mainly caused by the decomposition and release of organic K species, then the lost sharply increased when temperature reaches 1000℃, due to the abundant decomposition and evaporation of inorganic K, this means, the major part of K inherent the biomass is in the form of inorganic K salts like K_2CO_3, K_2SO_4 and K_2SiO_3 [17], which will not be decomposed until temperature is high enough. This result illustrates that the final temperature of the combustion significantly affects the retention of K content, the higher the final temperature, the less the K content that remained in the solid residues, especially at high temperatures like 1000°C.The final temperature influences the decomposition and evaporation of K species, besides, as the temperature increased, the biomass particles suffers significantly structure changes [18], with the breakage and collapse of porosity structure, more inner K content exposed, which accelerates the loss of K content.

3.2 Influence of heating rate on the retention of potassium

According to the reaction stages, five typical temperatures (300°C, 400°C, 600°C, 900°C and 1000°C, represents the low, medium and high temperatures) were selected to investigate the influence of heating rate on the retention of K in the residues, and the results are shown in Fig 3.

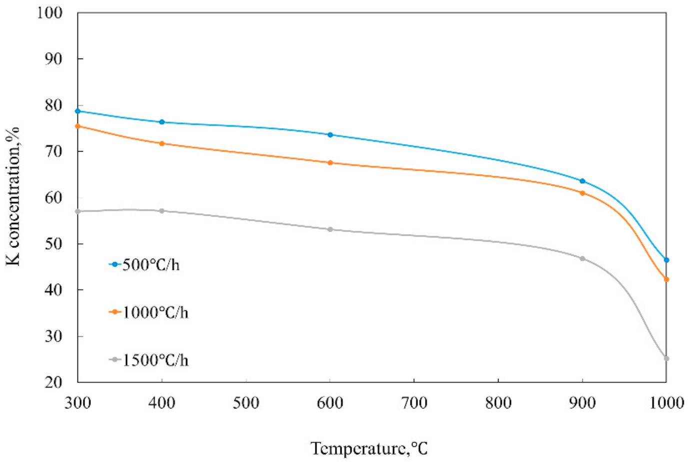

Fig 3. The change of K content (dry basis) with the change of heating rate

The figure shows the similar trends of the results under the three different heating rates, however, the K contents in the solid residues are different.

The K content in the solid residues under the same final temperature is quite close for the heating rate of 500°C/h and 1000°C/h. At 300°C, there is 78% of K left in the solid residues under the heating rate of 500°C/h, while it is 75% for the heating rate of 1000°C/h, as temperature increased, the K content deceased mildly for both curves. When temperature reaches to 1000°C, the K content drop to 46% and 42% for the heating rate of 500°C/h and 1000°C/h, respectively. The differences of K content under these two heating rates are small (<5%) for all the selected temperatures. However, when heating rate increases to 1500°C/h, the K content in the solid residues is much less compared to that of 500°C/h and 1000°C/h under the same temperature. At 300°C, there is only 57% of K retained in the residue, after a mild decrease at 400°C, 600°C and 900°C, steep decreased to 25% at 1000°C. And it can be seen that, under the same temperature, the different between the K content in the residues under these three heating rate is consistent, with <5% difference between the heating rate of 500°C/h and 1000°C/h, while it is 20% between the heating rate of 1000°C/h and 1500°C/h.

At a given final temperature, a higher heating rate implies that the sample can reaches that temperature in a shorter time [19], also a rapid heating rate can prevents the agglomeration of char structure and the condensation of fragments on the surface of char [12], which means, at lower temperature, the release of weakly-bonded K and organic K is quicker and more completely under high heating rate compared to low heating rate, while at higher temperature, the significant increase of char reactivates under high heating rate [20] would accelerate the decomposition of char-K and formation of KOH, K_2CO_3 and K_2SO_4 which would been released when temperature is high enough.

3.3 Influence of isothermal time on the retention of potassium

The same representative temperatures (300°C, 400°C, 600°C, 900°C and 1000°C) were used to investigate the influence of isothermal time on the retained K in the solid residues, and the tested results are shown in Fig 4.

The results show that when temperature is <900°C, the isothermal time does not affect the retention of K as much as that of heating rate. At 300°C and 400°C, the K content in solid residues are almost the same (with 75% and 72% respectively) under the isothermal time of 5 min and 10 min, while it is 69% under the isothermal time of 20 min; then all the curves are slowly decrease till to 900°C, during which, the difference of K content between the curves of 5 min and 10 min is within 5%, while it is nearly 10% between the curve of 10 min and 20 min. However, when final temperature reaches to 1000°C, the gaps between each other of the curves are significant, there is 54% of K left in the solid residues when isothermal time is 5min, while it is 42% and only 24% for the isothermal time of 10 min and 20 min respectively.

It can be seen that the influence of isothermal time on the retention of K is less significant compared to that of heating rate, especially at lower temperatures. Due to the same heating rate and final temperature, the combustion processes are the same for the different isothermal time conditions before they start the isothermal stage, the reaction mechanisms are almost identical for the three conditions. At low temperatures like 300°C and 400°C, the release of weakly bonded K and organic K are the main sources that cause the loss of K content [21, 22] , which occupies a small portion of total K content in biomass [5] , so the longer the isothermal time, the more completely release of organic K, however, the thermally stabled inorganic K will remain stable until the temperature is high enough to react. At temperature of 600°C, after the release of organic K, K is more likely to exists as char-K and inorganic K, the loss of K content at this temperature is negligible; while char-K can then react with C, S and Si to generate more inorganic K, like K_2CO_3, K_2SO_4 and K_2SiO_3. As temperature increase to 900°C and 1000°C, as aforementioned, more KOH released, while K_2CO_3 and K_2SO_4 start to decompose and evaporate, and the longer the isothermal time, the more inorganic K species reacted, leading to the less K content that remained in the solid residues.

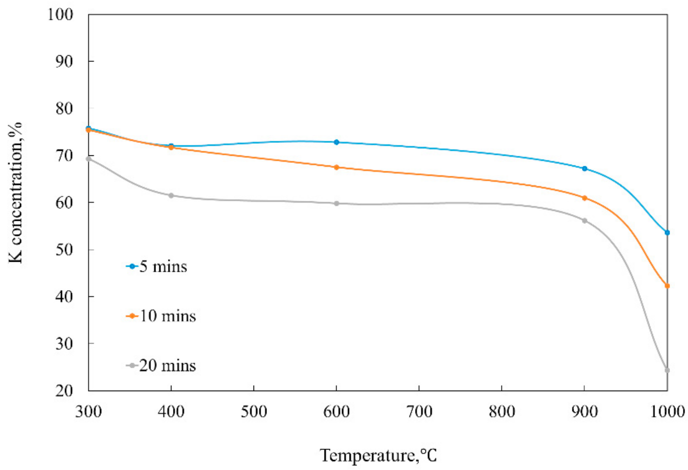

Fig 4. The change of K concentration (dry basis) with the change of isothermal time

4. Conclusion

This study experimentally investigated the influences of operating parameters on the retention of K content using high-temperature furnace balance system and ICP-OES. The results indicated that the final temperature is the factor that affect the retention of K content in solid residues the most, the higher the final temperature, the less the potassium that left. The influence of heating rate on the retention of K is consistent, the quicker the heating rate is, the less the K content that left in the solid residues. The effect of isothermal time on the retention of K is less important when temperature below 900°C, but much significant when temperature reaches 1000°C, and the longer the isothermal time, the less the potassium that retained due to the abundant decomposition and evaporation of inorganic potassium.

Morphology study will be carried out in the future to study how the operating parameters affect the particle structures, thereby influence the transition of potassium and related elements.

Acknowledgements

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