ISSN 2004-2965 Energy Proceedings, Vol. 18, 2021

International Conference on Applied Energy 2021
Nov. 29 - Dec. 2, 2021, Bangkok, Thailand
Paper ID: 079

Release and Transformation of Potassium During Biomass Gasification in a Fixed Bed Reactor With Steam-Oxygen Mixtures

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ABSTRACT

To investigate the release and transformation of fuel potassium during oxygen-steam gasification of biomass, wheat straw is gasified in a fixed-bed reactor system from 400 to 1000 °C. Weight measurement, elemental composition analysis and chemical fractionation analysis are performed. The influence of temperature on the release and transformation of inherent potassium is discussed. The results show that with the increase of gasification temperature, the water-soluble and NH4Ac-soluble K transform into other occurrence modes and the former plays a more important role. During the experiment, slagging is observed at 800 and 1000 °C. Further analysis conforms that the slagging at 1000 °C comprises of potassium silicate. The char obtained from 800 °C gasification is porous and the original fibrous structure of raw sample could be observed.

Keywords: potassium release, transformation, biomass gasification, oxygen-steam

1. INTRODUCTION

With the energy crisis of fossil energy and the related environmental problems, renewable and carbon-neutral energy is required [1]. The carbon peak and carbon neutral theory also strengthen people's demand for emission reduction. As the only carbon-based renewable energy source, biomass has attracted extensive attention. However, alkali metals in biomass especially potassium, could release into the gas phase, condensate on surfaces of downstream equipment and induce problems such as fouling, slagging [2]. These could cause safety hazards and reduce economic benefits. Meanwhile, the alkali metals remained in char would affect the subsequent utilization [3]. Therefore, it is of great importance to research the release and transformation of potassium during biomass gasification.

Among the utilization methods of biomass samples, gasification is flexible, efficient and environmentally friendly way and has attracted many scholars. Research on migration of alkali metals (K and Na) during gasification mainly focus on the traditional gasifying agent such as air, oxygen, steam or CO_2. Feng et al. found that during steam gasification potassium mainly releases in the form of inorganic salts and hydrates [4]. Zhao et al. compared potassium release between pyrolysis and CO_2 gasification and found that the relative content of potassium released into gas phase increases sharply and then gently as temperature increases, the proportion of potassium released in the earlier stage of gasification is higher than that of pyrolysis and potassium released in the later stage of gasification is almost the same as that of pyrolysis [5].

AlNouss et al. evaluated the technical-economic-environmental benefit during oxygen-steam gasification of biomass [6]. Bonilla et al. studied the influence of process parameters on the gasification with oxygen and steam mixtures and compared with air-steam gasification [7]. Zhou et al. studied the impact of bed materials on agglomeration behavior during oxygen-steam gasification using pine wood pellets and birch wood chips as fuel [8]. While the study on potassium transformation with steam-oxygen mixtures is rarely reported.

In this study, a fixed-bed reactor system is built up, and the release of potassium is evaluated quantitatively during gasification of wheat straw in the 400- 1000 °C interval. The transformation of occurrence mode of potassium in raw biomass and char is investigated through chemical fractionation analysis. The char is characterized by SEM-EDX method. The effect of gasification temperature is discussed in detail.

2. MATERIALS AND METHODS

2.1 Sample Preparation

In this study, wheat straw is selected for investigation. Wheat straw is collected from the rural areas of Xi'an, Shanxi Province, China. After grinding pretreatment, wheat straw is sieved and particles with

Selection and peer-review under responsibility of the scientific committee of the 13_{th} Int. Conf. on Applied Energy (ICAE2021).
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size of 150-250 μm are collected and dried in oven at 105 °C for 24 h for further gasification experiment. Part of the sample are sent to the Comprehensive Laboratory of Coalfield Geological Bureay (Xi'an Shaanxi Province) for proximate, ultimate and ash composition analysis. The ash composition analysis follows GB/T30725-2014. As for the potassium content determination, the biomass sample is dissolved by pressurized acidic digestion, and the content of potassium in the liquid sample is detected by inductively coupled plasma spectrometry (ICP-OES, Optima 7000DV, Perkin Elmer Co., USA). Details refer to our earlier study [9]. The results are shown in Table 1.

Table 1. Proximate and ultimate analysis

Ultimate analysis (wt%, ar)				
C	H	O	N	S
40.71	4.59	40.31	0.18	0.23
Proximate analysis (wt%, ar)				
FC	*V*	*A*	*M*	/
16.53	69.49	6.28	7.70	/
Main ash-forming elements (wt%, d)				
K	Si	Cl	Al	Ca
1.5729	1.2205	0.169	0.0475	0.3883

2.2 Gasification Experiment

Gasification experiments are conducted in a fixed-bed reactor system, which is shown in Fig. 1. From Fig. 1 it can be seen that the gasification experiments concludes steam generating system, gas supply system, reactor system and the exhaust gas treatment system. A cylindrical quartz reactor with an inner diameter of 45 mm and a height of 1000 mm is located in the electric heating zone of the furnace during gasification process. The quartz tube exposed outside the furnace and the steam generating path are wound with heating cable preventing condensation of water vapor. Dried biomass sample of 2±0.02 g is placed in the quartz cup with an external diameter of 40 mm which is slightly smaller than the diameter of the quartz reactor. A high-temperature quartz filter is laid beneath the biomass sample. Considering the porous structure of the bottom of the quartz cup, the permeability is ensured. And the surrounding wall of the quartz cup avoids the influence of the solid product being disturbed by the flow and the solid product can be collected easily.

The gasification experiments are performed in the 400- 1000 °C temperature range. First, the quartz reactor is heated from room temperature to the preset temperature with a heating rate of 10 °C/min. Then the mass flow meter of N_2 is supplied for about 10 min with a velocity of 100 mL/min to make sure the inert atmosphere inside the reaction system. The heat cable of the steam path is electrified, and the temperature is controlled around 150 °C with a temperature controller which is not shown in Fig .1. The injection pump is turned on with a supply of 120 uL/min to ensure the steam generation. About 20 min later the mass flow meter of oxygen is opened with a fixed gas velocity. The quartz cup is inserted into the constant temperature zone of the reactor and the biomass sample is gasified for about 20 min. At last, the steam generating system and oxygen supply system are turned off, the nitrogen supply system is turned on, and the quartz cup is withdrawn from the constant temperature for cooling. About 20 min later the nitrogen supply system is turned off. The cold char sample is weighted and collected for further study. The gasification experiments are repeated for at least two times to ascertain repeatability.

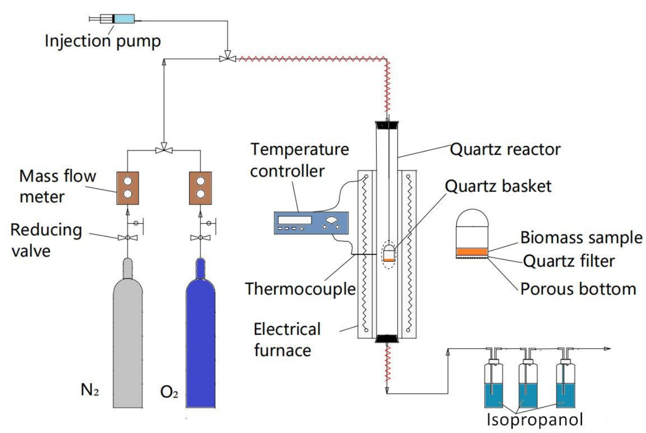

Fig.1 The fixed-bed reactor system of biomass gasification

2.3 Analysis

The release and transformation of potassium during biomass gasification is determined based on weight measurement, elemental analysis and chemical fractionation analysis. The details are described in our earlier study [9]. Sequential extractions are performed on samples with deionized water, CH_3COONH_4 (i.e. NH_4Ac) of 1.0 mol/L, and HCl of 1.0 mol/L. Raw and washed char samples are digested in a microwave

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digestion system (Multiwave 3000, Anto Paar, Austria). Finally the potassium content in the solution is measured by ICP-OES. Thus the potassium distribution among deionized water, NH4Ac liquid, HCl liquid and left solid are determined. All the measurements are repeated at least two times for repeatability.

Scanning electron microscope (SEM-EDX, SU3500, Tianmei Scientific Instruments Co., Ltd., China) is selected for observation of microscopic morphology and determination of relative element content to better analyze the potassium distribution in char sample.

3. RESULTS AND DISCUSSION

3.1 Potassium Release to the Gas Phase

The release ratio of potassium during gasification is shown in Fig. 2. The maximum standard deviation reaches at 1000 °C, and the absolute value is below 1.5%. Only around 7.8% of potassium is released into the gas phase at 400 °C, and as the gasification temperature rises, the release ratio of potassium increases. The release ratio reaches around 60% at 1000 °C. Further analysis shows that the release rate increases faster in the temperature range of 800-1000 °C compared to that from 400- 800 °C. Thus high temperature favors potassium release.

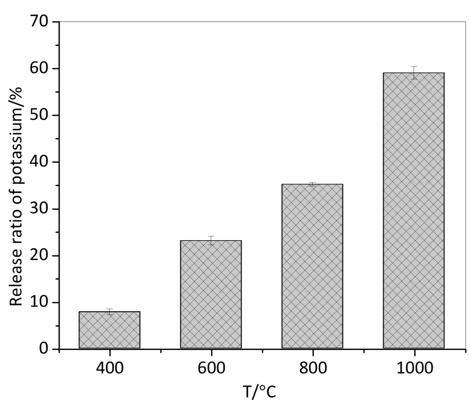

Fig. 2. Release ratio of potassium during gasification

3.2 Potassium Transformation during Gasification

Generally speaking, the alkali metals extracted by water are salts and hydrated ions, that is, water-soluble salts and substances that are bound by chemical absorption; NH_4Ac liquid extracts alkali that exists in biomass in the form of organic matter; HCl liquid extracts substances that exist in the form of soluble sulfates, carbonates, etc. The residues that cannot be dissolved by the above reagents are insoluble substances like sulfite, sulfide and silicate [10]. The transformation of potassium during biomass gasification is represented as the potassium distribution ratio shown in Fig. 3. It can be seen that water-soluble K always occupies the main content in raw wheat straw sample and chars. More than 80% of the potassium in raw wheat straw is water-soluble K which is followed by NH_4Ac-soluble K. Only limited potassium is insoluble in raw wheat straw sample. The relative content of water-soluble and NH_4Ac-soluble K in char decrease as the gasification temperature rises. While the content of HCl-soluble and insoluble K has an opposite trend, that is, the higher temperature, the lower relative content in the char. It can be inferred that the water-soluble and NH_4Ac-soluble K transform into other occurrence modes and the former plays a more important role.

However, the specific conversion path is unknown. For example, the water-soluble K could be transformed into HCl-soluble K directly and could also be transformed into NH_4Ac-soluble K. And part of NH_4Ac-soluble K is then converted into HCl-soluble K as reactions continue, while the left part remains NH_4Ac-soluble. Considering the various compounds in NH_4Ac-soluble form such as char-COOK and char-O-K, the corresponding occurrence modes of K in NH_4Ac-soluble section could also change. Hence further characterization methods are needed for analysis.

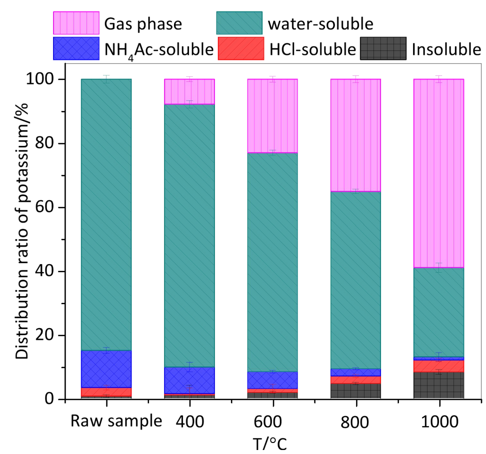

Fig. 3. Distribution ratio of potassium at various temperature

During the experiment, slagging is observed at 800 and 1000 °C and the microscopic morphology of char under 500 times magnification is shown in Fig. 4. It can be observed that there exists partial melting at 800 °C with smooth sphere, while obvious slagging appears at 1000 °C. The EDX result of the part marked in red is shown in Table 2. Only oxygen, silicon and potassium atoms are found and thus the compound present is potassium silicate. Besides, the char obtained from

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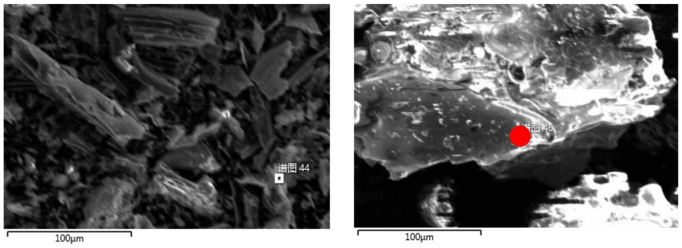
800 °C gasification is porous and the original fibrous structure of wheat straw could be observed.



(a) 800 °C (b) 1000 °C

Fig. 4. Distribution ratio of potassium at various temperature

Table 2. EDX result of char obtained from experiment at 1000 °C

O	Si	K
29.62	22.53	47.84

4. CONCLUSIONS

In this study, the release and transformation of fuel potassium during gasification in a fixed bed reactor with steam-oxygen mixtures are investigated using chemical fractionation analysis and characterization methods. The influence of gasification temperature on release and transformation of potassium is researched, and the following conclusions are obtained:

(1) With the increase of gasification temperature, the water-soluble and NH_4Ac-soluble K transform into other occurrence modes and the former plays a more important role.

(2) During the experiment, slagging is observed at 800 and 1000 °C. Further analysis conforms that the slagging at 1000 °C comprises of potassium silicate.

(3) The char obtained from 800 °C gasification is porous and the original fibrous structure of raw sample could be observed. While the fibrous structure disappears on surface of char obtained from 1000 °C gasification.

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