

# Research on Release and Transformation of Fuel K during Biomass Gasification

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## ABSTRACT

To investigate the release and transformation of fuel K during air gasification of biomass, wheat straw, corn stalk and rice straw are gasified in a fixed-bed reactor system from 400 to 1000 °C. Weight measurement, elemental composition analysis, and chemical fractionation analysis are performed. The influences of release of Cl, fuel type and gasification temperature on the release of K are discussed. The results show that for all biomass fuels, the release ratio of K and Cl increases with gasification temperature. In the 400-600 °C interval, the release of K and Cl increases gently and sharply respectively, and the trend from 600 to 1000 °C is the opposite. From the release ratio of K and Cl together with the distribution ratio of water-soluble K, it can be concluded that part of water-soluble K transforms to gas phase in the form of KCl in the 600-1000 °C interval.

**Keywords:** potassium release, transformation, biomass gasification

## 1. INTRODUCTION

With the energy crisis of fossil energy and the awareness of environmental protection, biomass has attracted increasing attention for its property of renewable and carbon-neutral [1]. However, there exist massive alkali metals which can be released to the gas phase during gasification, condensate on surfaces of downstream equipment and induce problems of fouling, slagging and high temperature corrosion [2]. Meanwhile, a large amount of alkali metals in char will affect subsequent utilization [3]. Therefore, it is of great importance to study the release and transformation of alkali metals during gasification of biomass.

Researches on migration of alkali metals (K and Na) during utilization of biomass mainly focus on pyrolysis and combustion nowadays. Zhao et al. studied the transformation of K during fast-pyrolysis of rice straw [4].

It was concluded that a relatively high Cl content would promote release of K in the form of KCl [5, 6]. However, only limited attention has been focused on the transformation of occurrence mode of K and the relation of K and Cl released during air gasification of biomass.

In this study, a fixed-bed reactor system is built up, and the release of K is evaluated quantitatively during gasification of wheat straw, corn stalk and rice straw in the 400-1000 °C interval. The transformation of occurrence mode of K in raw biomass and char is investigated at different temperature through chemical fractionation analysis. The release of Cl to gas phase is analyzed qualitatively and the relation between the release of K and Cl is illustrated. The effects of fuel type, gasification temperature are discussed in detail.

## 2. MATERIALS AND METHODS

### 2.1 Sample Preparation

In this study, wheat straw, corn stalk and rice straw are used for investigation. Wheat straw is collected from the rural areas of Xi'an, Shaanxi Province, China, and the others come from Jiangsu. After being milled, sieved to 150-250 μm and dried at 105 °C for 24 h, samples are sent to the gasification experiment and the chemical fractionation analysis. The biomass samples are sent to the Comprehensive Laboratory of Coalfield Geological Bureau (Xi'an Shaanxi Province) for proximate and ultimate analyses, and ash composition analysis. And the ash preparation is followed ASTM E830 at 575 °C. After being dissolved by pressurized acidic digestion, the potassium contents in the solutions are measured by inductively coupled plasma spectrometry, and the content of chlorine is detected using ion chromatography. Details refer to our earlier study [7].

The fuel properties of biomass samples are listed in Table 1. For the content of K and Na, the standard

deviation is calculated from two to three replicates of measurements.

Table 1. Fuel properties of biomass samples

	Wheat straw	Rice straw	Corn stalk
Proximate analysis(wt%, dry basis)			
A	6.80	12.24	7.09
V	75.29	70.97	74.89
FC	17.91	16.79	18.02
Ultimate analysis(wt%, dry basis)			
C	44.11	32.67	46.18
H	4.97	1.66	4.89
O	43.67	52.36	40.50
N	0.20	0.87	1.09
S	0.25	0.20	0.25
Cl	0.664±0.004 <sup>a</sup>	0.738±0.003	0.540±0.003
Main ash-forming elements(wt%, dry basis)			
Si	1.22	5.99	1.19
K	2.990±0.016	1.225±0.001	3.035±0.016
Molar ratios of the main ash-forming elements(mol/mol)			
K/Si	1.760	0.147	1.831
Cl/K	0.244	0.662	0.195

<sup>a</sup> standard deviation

## 2.2 Gasification Experiment

Gasification experiments are conducted in a fixed-bed reactor system, which is illustrated in Fig. 1. A quartz reactor that has an inner diameter of 45 mm is located in an electric heating furnace. A dry biomass sample of 2±0.02 g is placed in a quartz cup with an external diameter of 40 mm. A high-temperature quartz filter is laid beneath biomass sample and the bottom of the quartz cup is equipped with several pores to insure enough permeability.

The gasification experiments are performed from 400 to 1000 °C. First, the quartz reactor is heated to a preset temperature. Then, the mass flow meter of N<sub>2</sub> is opened, and the quartz reactor is purged by the pure N<sub>2</sub> for about 10 min to make sure the whole reactor is in an nitrogen atmosphere. Later, the mass flow meter of O<sub>2</sub> is opened and the flow rates of gases are regulated to preset values to simulate air atmosphere. The quartz cup is inserted into the constant temperature zone of the reactor, and the biomass sample is gasified for 20 min. At last, the quartz cup is withdrawn to the cooling section of quartz reactor and the mass flow meter of O<sub>2</sub> is turned off. Thus the char sample can be cooled by the cold N<sub>2</sub> and the surrounding environment. The cold char sample is collected and weighted. For each type of biomass sample, gasification experiments are repeated three times to ascertain repeatability.

## 2.3 Analysis

The release and transformation of potassium during biomass gasification is determined based on weight measurements, elemental composition analysis, and chemical fractionation analysis. The details are described in our earlier study [7]. Sequential extractions are performed on samples with deionized water, CH<sub>3</sub>COONH<sub>4</sub> (i.e. NH<sub>4</sub>AC) of 1.0 mol L<sup>-1</sup>, and HCl of 1.0 mol L<sup>-1</sup>. Raw and washed char samples are digested in a microwave digestion system (Multiwave 3000, Anto Paar, Austria). Finally the potassium contents in the solutions are measured by an inductively coupled plasma-optical emission spectroscopy (ICP-OES, Perkin Elmer, USA), and water-soluble K, NH<sub>4</sub>Ac-soluble K (ion-exchangeable K), HCl-soluble K, and insoluble K can be obtained. The content of water-soluble Cl is obtained by ion chromatography (IC 930, Xi'an Shengjing Biotechnology Company, China). All the measurements are repeated three times for repeatability.

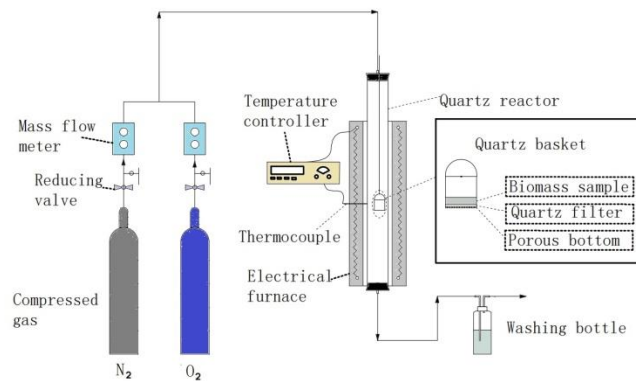


Fig. 1. The fixed-bed reactor system of biomass gasification.

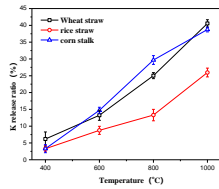
## 3. RESULTS AND DISCUSSION

### 3.1 Release of K and Cl to the Gas Phase

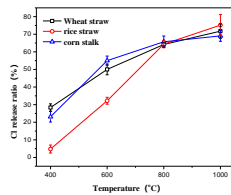
Previous studies have shown that more than 90% of Cl in biomass exists as water-soluble, and there exists a good correlation between the total Cl content and the water-soluble Cl content in biomass [8-10]. Thus the water-soluble Cl content is used to represent the total Cl content in the char samples.

Fig.2a displays the K release of three biomass samples. The ratio of K release to gas phase rises with temperature for all three biomass samples. The ratio of K released increases gently in the 400-600 °C interval and sharply in the 600-1000 °C interval. This trend in this study is quite similar to that of Knuden et al. [11], which indicates that increment of temperature induces the massive release of K, and the phenomenon is more obvious above 700 °C.

Fig.2b illustrates the Cl released from gasification of three biomass samples. As the temperature rises, the Cl release increases. Cl release ratio increases sharply from 400 to 800 °C, increases gently from 800 to 1000 °C, and reaches about 70% at 1000 °C for all biomass samples. Thus the Cl release is mainly divided into two stages: the rapid release in the 400-800 °C interval, and the slow release in the 800-1000 °C interval. This trend is similar to the phenomenon observed by Scott [12].



(a) Release of K



(b) Release of Cl

Fig. 2. Release of K and Cl at different temperature.

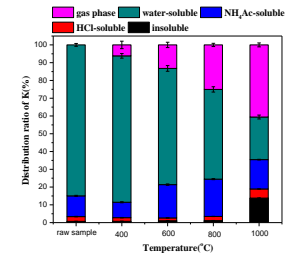
Comparing Fig.2a and Fig.2b, it can be seen that in the 600-800 °C interval, release ratio of K and Cl increases sharply for all biomass samples, indicating that the release of K is promoted by release of Cl from 600 to 800 °C. This is similar to the conclusion of Wei et al. [13, 14]. It is also found that Cl release ratio is higher than that of K in the 400-1000 °C interval for all these three biomass samples, illustrating that KCl is not the only form of Cl released. Bjorkman et al. found that besides released in the form of KCl, Cl is also released as HCl [15].

From Table 1 it can be seen that for corn stalk, the molar ratio of K/Si is the highest and that of Cl/K is the lowest among three biomass samples. Thy P et al. illustrated that silicon would react with K, resulting in the immobilize of K in the char under high temperature [4]. John et al. pointed out that the release of alkali metals could be promoted for biomass samples with high Cl content when the temperature is high than 500 °C [16]. Thus the positive effect of Si is stronger than the promoting effect of Cl on the release of K, and the release trend of K from 800 to 1000 °C for rice straw can be explained.

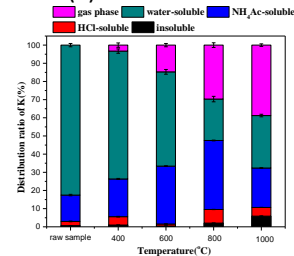
### 3.2 Transformation of K during Gasification

The transformation of K during biomass gasification is represented as the distribution ratio of K in the solid phase (different occurrence modes) and gas phase, which is shown in Fig.3. The occurrence mode of potassium in the raw biomass sample and residual char is obtained following details in our earlier study [7]. It can be found that the water-soluble K is more than 80% and the summation of HCl-soluble and insoluble K is less than 5% for all biomass samples. Moreover, for all biomass samples, the distribution ratio of water-soluble K decreases, while the ratio of insoluble K and K released to gas phase increases as the temperature rises, indicating that water-soluble K could be transformed into gas-phase K and the insoluble-K is less likely transformed to other forms of occurrence of K.

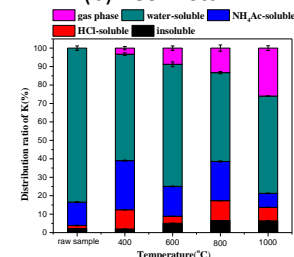
From 600 to 1000 °C, the distribution ratio of water-soluble K decreases for all these three biomass samples with the maximum reduction being 41% around. Since the water-soluble K is the easiest to be released among all the occurrence modes of K and KCl is soluble in water, it can be concluded that part of water-soluble K transforms to gas phase in the form of KCl in the temperature of 600 to 1000 °C. And this trend is verified by the release ratio of K and Cl in the 600-1000 °C interval.



(a) Wheat straw



(b) Corn stalk



(c) Rice straw

Fig. 3. K release at different gasification temperatures.

#### 4. CONCLUSIONS

In this study, the release and transformation of fuel K during air gasification of wheat straw, corn stalk and rice straw in a fixed-bed system are investigated. The influences of release of Cl, fuel type and gasification temperature on the release of K are discussed. The following conclusions are obtained:

(1) With the increase of gasification temperature, the ratio of K and Cl released to gas phase increases.

(2) In the 400-600 °C interval, the release of K and Cl increases gently and sharply respectively, and the trend from 600 to 1000 °C is the opposite.

(3) From the release ratio of K and Cl together with the distribution ratio of water-soluble K, it can be concluded that part of water-soluble K transformed to gas phase in the form of KCl in the 600-1000 °C interval.

#### ACKNOWLEDGEMENT

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#### REFERENCE

- [1] Cornea TM, Dima M. biomass energy - a way towards a sustainable future. *Environmental Engineering and Management Journal*. 2010;9:1341-5.
- [2] Baxter LL, Miles TR, Miles TR, Jenkins BM, Milne T, Dayton D, et al. The behavior of inorganic material in biomass-fired power boilers: field and laboratory experiences. *Fuel Processing Technology*. 1998;54:47-78.
- [3] Wornat MJ, Hurt RH, Yang NYC, Headley TJ. STRUCTURAL AND COMPOSITIONAL TRANSFORMATIONS OF BIOMASS CHARS DURING COMBUSTION. *Combustion and Flame*. 1995;100:133-45.
- [4] Zhao H-b, Song Q, Wu X-y, Yao Q. Study on the Transformation of Inherent Potassium during the Fast-Pyrolysis Process of Rice Straw. *Energy & Fuels*. 2015;29:6404-11.
- [5] Johansen JM, Jakobsen JG, Frandsen FJ, Glarborg P. Release of K, Cl, and S during Pyrolysis and Combustion of High-Chlorine Biomass. *Energy & Fuels*. 2011;25:4961-71.
- [6] Knudsen JN, Jensen PA, Dam-Johansen K. Transformation and release to the gas phase of Cl, K, and S during combustion of annual biomass. *Energy & Fuels*. 2004;18:1385-99.
- [7] Deng L, Ye J, Jin X, Che D. Transformation and release of potassium during fixed-bed pyrolysis of biomass. *Journal of the Energy Institute*. 2018;91:630-7.

[8] Okuno T, Sonoyama N, Hayashi J, Li CZ, Sathe C, Chiba T. Primary release of alkali and alkaline earth metallic species during the pyrolysis of pulverized biomass. *Energy & Fuels*. 2005;19:2164-71.

[9] Dayton DC, Jenkins BM, Turn SQ, Bakker RR, Williams RB, Belle-Oudry D, et al. Release of inorganic constituents from leached biomass during thermal conversion. *Energy & Fuels*. 1999;13:860-70.

[10] Jenkins BM, Bakker RR, Wei JB. On the properties of washed straw. *Biomass & Bioenergy*. 1996;10:177-200.

[11] Knudsen J N JPA, Dam-Johansen K. Transformation and release to the gas phase of Cl, K and S during combustion of annual biomass. *Energy & Fuels*. 2004;18:1385-99.

[12] Turn SQ. Chemical equilibrium prediction of potassium, sodium, and chlorine concentrations in the product gas from biomass gasification. *Industrial & Engineering Chemistry Research*. 2007;46:8928-37.

[13] Wei XL, Schnell U, Hein KRG. Behaviour of gaseous chlorine and alkali metals during biomass thermal utilisation. *Fuel*. 2005;84:841-8.

[14] van Lith SC, Jensen PA, Frandsen FJ, Glarborg P. Release to the gas phase of inorganic elements during wood combustion. Part 2: Influence of fuel composition. *Energy & Fuels*. 2008;22:1598-609.

[15] Bjorkman E, Stromberg B. Release of chlorine from biomass at pyrolysis and gasification conditions. *Energy & Fuels*. 1997;11:1026-32.

[16] Olsson JG, Jaglid U, Pettersson JBC, Hald P. Alkali metal emission during pyrolysis of biomass. *Energy & Fuels*. 1997;11:779-84.