



# On-line measurement and kinetic studies of sodium release during biomass gasification and pyrolysis



Zhen Zhang<sup>a</sup>, Jing Liu<sup>a,b,\*</sup>, Fenghua Shen<sup>a</sup>, Yingju Yang<sup>a</sup>, Feng Liu<sup>a</sup>

<sup>a</sup>State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, Wuhan 430074, China

<sup>b</sup>Shenzhen Institute of Huazhong University of Science and Technology, Shenzhen 518000, China

## HIGHLIGHTS

- Temporal release of sodium from sawdust gasification and pyrolysis was measured.
- Influences of temperature and atmosphere on sodium release were investigated.
- Chlorine was more propitious to sodium release in gasification than pyrolysis.
- Thermodynamic equilibrium calculations were conducted to identify sodium species.

## ARTICLE INFO

### Article history:

Received 12 January 2016

Received in revised form 15 March 2016

Accepted 16 March 2016

Available online 24 March 2016

### Keywords:

Sodium  
Release behavior  
Biomass  
On-line measurement  
Gasification

## ABSTRACT

The release of sodium during biomass gasification and pyrolysis in fluidized bed was systematically investigated based on an on-line measurement system. The temperature and atmosphere had strong influences on sodium release behavior. The pyrolysis atmosphere was conducive to the release of sodium than the CO<sub>2</sub> gasification atmosphere at 900 °C. The overall kinetic parameters of sodium release during two thermal conversion processes were obtained based on the experimental results of instantaneous sodium concentration in flue gas and inverse method. Furthermore, the influence of chlorine on sodium release was studied based on the on-line measurement system. The promoting effect of chlorine on Na release in CO<sub>2</sub> gasification was much more obvious than pyrolysis. Thermodynamic equilibrium calculations were conducted to identify the sodium species during biomass gasification and pyrolysis. The formation of Na<sub>2</sub>CO<sub>3</sub> (s, l) mainly accounted for the lower release percentage of sodium in CO<sub>2</sub> gasification than pyrolysis.

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## 1. Introduction

The gasification/pyrolysis is considered as a crucial biomass utilization alternative, offering economic benefit through the production of useful fuel gases, char and chemicals [1–4]. The release of alkali metals during biomass gasification and pyrolysis can cause serious damage to thermal equipment materials, due to fouling, slagging and agglomeration, which are mainly ascribed to low melting points and high reactivity of alkali metals [5–9]. The release of alkali metals also has an influence on the energy and mass flows in furnaces. In fluidized bed, a high-level vaporization of alkali metals can give rise to agglomeration and sintering of bed material and consequent defluidization [10–13]. Therefore, the detailed knowledge on the behavior of sodium (Na) release during gasification and pyrolysis is needed to better understand

the behavior and minimize the damage through choosing the optimum control strategies.

The release behaviors of sodium during biological waste gasification and pyrolysis have been investigated previously by analysis of different residues produced by gasification and pyrolysis under different conditions [14–18]. Long et al. [17] investigated the release characteristics of sodium during biomass pyrolysis and steam gasification using a quartz fixed-bed reactor. The results indicated that the pyrolysis atmosphere was propitious to Na release than the steam gasification atmosphere at 900 °C. Lane et al. [18] used a laboratory-scale fixed-bed reactor to study the release of Na during pyrolysis and gasification of algal biomass under isothermal conditions ranging. The results indicated that the chlorine was released together with the alkali metals primarily by sublimation of NaCl and the volatilization of carboxylate sodium could cause Na release from algae at low temperatures. However, the release behaviors of sodium during biological waste gasification and pyrolysis cannot be satisfactorily interpreted since

\* Corresponding author at: State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, Wuhan 430074, China.

the analyzing residues methods can only give the sodium release integrated over a long period, thus disregarding the possible peaks of sodium release. Therefore, the continuous on-line measurements are necessary to identify the temporal evolution processes of sodium release during biological waste gasification and pyrolysis.

To date, there is little detailed understanding of the temporal evolution of sodium during biological waste gasification and pyrolysis. The kinetic studies are also needed to identify the dynamic characteristics of sodium release during biological waste gasification and pyrolysis. The on-line analysis system based on inductively coupled plasma optical emission spectroscopy (ICP-OES) can measure the temporal concentrations of trace elements in flue gas quantitatively, which has been identified as a reliable technique [19–21]. In our previous work [22], the on-line analysis system has been successfully applied in the study of arsenic release behavior during coal combustion and gasification processes. Moreover, chlorine (Cl) content is also an important parameter that affects Na release during thermal conversion processes. However, up to now, there is an absence of detailed knowledge of the influence of chlorine on Na release during biological waste gasification and pyrolysis based on on-line measurement technique.

The objective of this study is to develop an on-line analysis system for measuring quantitatively the concentration profiles of sodium in flue gas, and identify the behavior of sodium release during gasification and pyrolysis of biological waste. The overall kinetic parameters of sodium release during two thermal conversion processes are determined based on the results of on-line analysis and the inverse method. The influence of chlorine on Na release during gasification and pyrolysis is also investigated. Thermodynamic equilibrium calculations were conducted to identify the sodium species during biological waste gasification and pyrolysis.

## 2. Experimental section

### 2.1. Fluidized bed and on-line sodium measurement system

The schematic diagram of the experimental setup is shown in Fig. 1, consisting of a fluidized bed and an on-line sodium analysis

system. The bubbling fluidized bed reactor is a 1500 mm high chamber with inner diameter of 40 mm [23]. The upper section (1100 mm) of the reactor is for reaction, and the lower section (400 mm) is for preheating. The fluidization gas was introduced into the reactor from the bottom and pre-heated by the lower section of the reactor. The fluidizing gas was argon (Ar) for pyrolysis, and 20% CO<sub>2</sub>/80% Ar for gasification. The bed material was composed of quartz sand with particle diameter of 0.55–0.83 mm (initial bed height 35 mm).

The on-line analysis system based on ICP-OES (Spectro Arcos Sop, Germany) was developed to measure sodium concentration in flue gas continuously and quantitatively. The torch employed for on-line measurement is a quartz demountable torch with an injector inner diameter of 1.8 mm. This torch can sustain a higher coolant gas flow, which is necessary for a high power to maintain the stability of plasma under different conditions. A small cyclone was used to remove large particulates from the outlet gas of the fluidized bed. The gas to analyze is aspirated through a set of pumps including a primary sampler (membrane pump) and a secondary sampler (peristaltic pump). The sample line is operated at a temperature of 200 °C to avoid water condensation. The sampling system is able to sample gaseous sodium and sodium in ultrafine particles. The high temperature of the plasma makes the analysis system capable to excite those gaseous species and small particles. The sample gas flow rates were optimized based on a balance of signal intensity and background noise. The optimum sample gas flow rate is 0.14 L min<sup>-1</sup> for measuring sodium concentration.

### 2.2. Quantitative calibrations and experimental sample

Performing direct calibration is important because few elements are commercially available in the form of volatile (or gaseous) compounds. Calibration is achieved by introducing a standard aerosol, prepared in-situ using an ultrasonic nebulizer (USN, Cetac U5000AT+). It improves the limit of detection by increasing the analyte transport efficiency and stripping the solvent from the aerosol [24]. The analytical wave length used for the detection of Na is 588.995 nm. The standard aerosols were prepared in-situ with concentrations of 0, 0.1, 0.2, 1 and 2 mg m<sup>-3</sup>

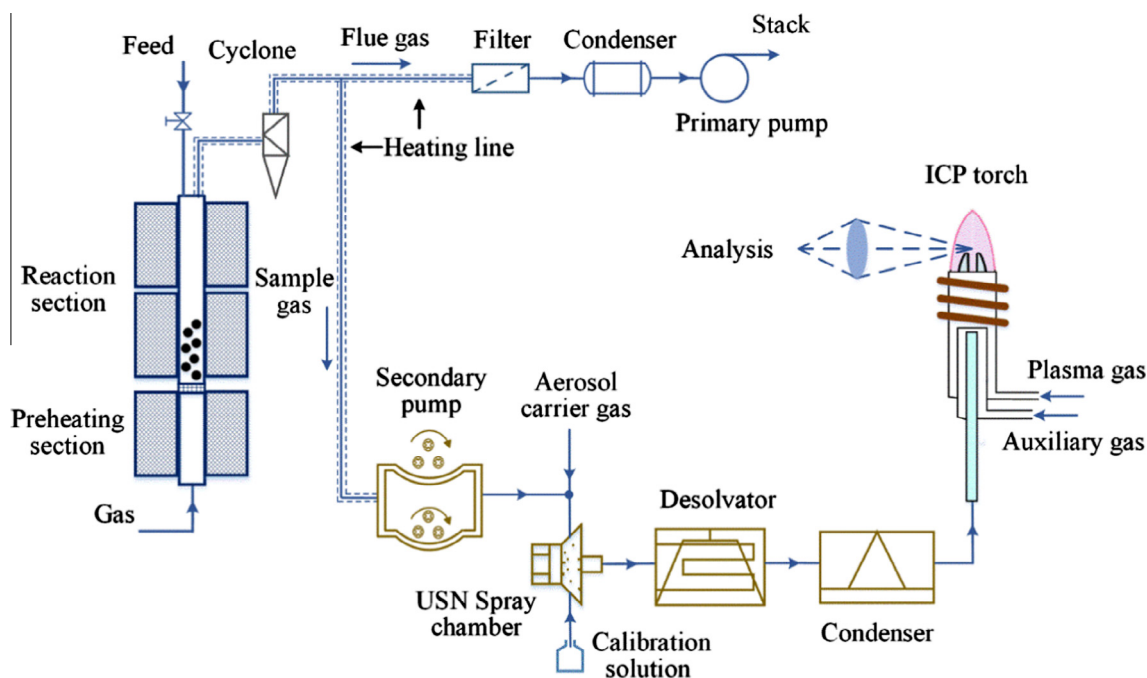


Fig. 1. The schematic diagram of the experimental setup.

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