



# Effects of inherent alkali and alkaline earth metallic species on biomass pyrolysis at different temperatures



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## HIGHLIGHTS

- Inherent AAEMs affected distribution of pyrolysis product at different temperatures.
- Water–gas shift reaction was enhanced by inherent AAEMs.
- Decomposition of levoglucosan was accelerated significantly by inherent AAEMs.
- Breakage and restructuring of hetero atoms of tar were promoted by inherent AAEMs.

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## ABSTRACT

This work aimed to investigate effects of inherent alkali and alkaline earth metallic species (AAEMs) on biomass pyrolysis at different temperatures. The yield of CO, H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> was increased and that of CO<sub>2</sub> was suppressed with increasing temperature. Increasing temperature could also promote depolymerization and aromatization reactions of active tars, forming heavier polycyclic aromatic hydrocarbons, leading to decrease of tar yields and species diversity. Diverse performance of inherent AAEMs at different temperatures significantly affected the distribution of pyrolysis products. The presence of inherent AAEMs promoted water–gas shift reaction, and enhanced the yield of H<sub>2</sub> and CO<sub>2</sub>. Additionally, inherent AAEMs not only promoted breakage and decarboxylation/decarbonylation reaction of thermally labile hetero atoms of the tar but also enhanced thermal decomposing of heavier aromatics. Inherent AAEMs could also significantly enhance the decomposition of levoglucosan, and alkaline earth metals showed greater effect than alkali metals.

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## 1. Introduction

The rapid population growth, deteriorating environment and energy crisis make researches related to renewable and alternative fuel resources extremely essential. Lignocellulosic biomass, which is the only carbon-based, clean and carbon-neutral renewable energy resource, has great prospects of substituting for traditional fossil fuels to meet above challenges.

Pyrolysis has been proven to be an efficient and appropriate technological route for biomass conversion to produce value-added chemicals and bio-fuels (Borges et al., 2014; Zhang et al., 2014); especially fast pyrolysis which prefers to convert biomass to bio-oils is particularly interesting. Moreover, pyrolysis is also the first and fundamental step in gasification, combustion and other thermochemical conversion processes for biomass

exploitation. Accordingly, there are extensive research motivations for achieving in-depth understanding of biomass pyrolysis for technology development and optimization. However, the behavior of biomass pyrolysis is very complex depending on varieties of biomass feedstock and reaction conditions, and currently it is still a way from a full unraveling.

Minerals are generally considered as an important factor in biomass pyrolysis. Unlike coal, lignocellulosic biomass especially agricultural residue (straw residues, husk residues etc.) contains considerable amounts of alkali and alkaline earth metallic species (AAEMs) such as sodium, potassium, calcium, magnesium, etc., which are the integral nutrient constituents of biomass. Many studies (Jensen et al., 2000; Keown et al., 2005; Long et al., 2012) found the AAEMs were prone to be volatilized during thermal conversion of biomass and considerable parts of AAEMs would release in the form of gaseous. The released AAEMs and remaining AAEMs would be involved in volatile–volatile and volatile–char interactions (Zolin et al., 2001). Thus, biomass pyrolysis process is

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possible to be significantly altered via the catalytic alteration of several thermolysis reactions by AAEMs.

Extensive work has been conducted in the last two decades to understand the role of internal AAEMs in biomass pyrolysis (Di Blasi et al., 2009; Jensen et al., 1998; Mourant et al., 2011; Patwardhan et al., 2010; Raveendran et al., 1995; Zolin et al., 2001). Raveendran et al. (1995) and Di Blasi et al. (2009) found the presence of both internal and added AAEMs could promote the formation of bio-char and gaseous species at the expense of bio-oil yield in biomass pyrolysis. Mourant et al. (2011) studied the fast pyrolysis of mallee wood using a fluidized bed reactor, and found the presence of AAEMs did not result in significant changes in the yields of bio-char and bio-oil, but drastically affect the bio-oil properties (e.g. viscosity). Vamvuka et al. (2006) studied the effect of inorganic constituents on the thermal behavior of low rank coals, as well as agricultural and forestry by-products during pyrolysis and combustion processes. They pointed out Ca, Mg, K and Si minerals had a small effect on the reactivity of biomass pyrolysis, and these minerals acted as inert materials inhibiting the combustion rate of both biomass and coal samples. Patwardhan et al. (2010) studied the effect of AAEMs salts on pyrolysis of cellulose. They pointed out that the AAEMs salts accelerated the decomposition reactions, and promoted to the formation of low molecular weight species from cellulose.

However, there is a lack of systematical investigation on effects of inherent alkali metals and alkaline earth metals on biomass pyrolysis at different temperatures. Additionally, Biomass washing by water or acids is always considered as an available method to remove AAEMs from biomass, and our previous work (Jiang et al., 2013) indicated water and HCl washing was a good way to separately evaluate the catalytic effects of inherent alkali metals and alkaline earth metals on biomass pyrolysis. Thus, the main purpose of this paper was to investigate the catalytic effect of inherent AAEMs on yield and property of biomass pyrolysis products at different temperature by using water and HCl washing method.

In this study, rice husk was selected as the feedstock due to its higher content of AAEMs as well as abundance in China and other Asian countries. Rice husk was washed by water and HCl solution and pyrolyzed by using an updraft quartz reactor at the temperatures of 500–900 °C. The yield and composition of non-condensable gases were determined by using gas chromatography (GC), and the tar was analyzed by using gas chromatography – mass spectrometry (GC–MS) and ultraviolet fluorescence spectroscopy (UV-F), finally the different effect of inherent alkali metals and alkaline earth metals on yield and property of biomass pyrolysis products at different temperatures were discussed.

## 2. Methods

### 2.1. Material

A typical Chinese agricultural residue – rice husk harvested at Wuhan area, Hubei province was pre-dried in the sun, and then pulverized and sieved. The fractions of particle size between 125 and 210  $\mu\text{m}$  were selected and dried in an oven at 105 °C for 24 h using for experiments.

### 2.2. Washing procedure

Biomass sample was washed by deionized water and HCl agent (analytically pure, Sinopharm chemical reagent Co., Ltd, Shanghai, diluted to 5 wt% with deionized water). The washing procedure has been reported in details elsewhere (Jiang et al., 2013). Briefly, biomass sample was immersed in washing agents (1 g of sample per 10 ml agent), stirred for 2 h at ambient temperature ( $25 \pm 3$  °C),

filtered and rinsed with deionized water until neutral, dried in an oven at 105 °C for 24 h, then collected and sealed in desiccators.

### 2.3. Sample analysis

The ultimate and proximate analyses of samples were respectively analyzed by EL-2 analyzer (Vario Company, Germany) and TGA-2000 (Las Navas Instruments, Spain). Table 1 shows the analysis data.

Inherent AAEMs amount of samples was quantified by using inductively coupled plasma mass spectrometry (ICP-MS) of which testing procedure had been described elsewhere (Long et al., 2012). Briefly, the sample was digested by 1 ml HF (38 wt%), 2 ml H<sub>2</sub>O<sub>2</sub> (30 wt%) and 10 ml HNO<sub>3</sub> (65 wt%) mixture agents which all were analytically pure and bought from Sinopharm chemical reagent Co., Ltd, Shanghai using a microwave digestion system. The digestion mixture was then measured by ICP-MS. The quantification was repeated for three times to ensure accuracy of the data. Table 2 shows the quantified data.

### 2.4. Experimental procedure

The pyrolysis experiments were carried out in a spout-fluid bed reactor (Fig. 1). The experimental system was composed by gas feeding system, biomass feeding system, reaction zone, tar capture system as well as gas monitor and collection system. The quartz reactor included two parts: bottom gas preheat zone and top spout-fluid reaction zone (inner diameter of 5 mm, 26 mm and length of 300 mm, 300 mm, respectively). The high purity quartz wool (purity > 99.99%, ultimate temperature of 1600 °C) was placed on the flared area of the reactor, and the quartz sieve was placed on the upper of the reactor, to ensure the particles staying in the reaction zone.

$2.00 \pm 0.05$  g of biomass was pre-loaded into the biomass feeder. The reactor was heated to the desired temperature of 500–900 °C, and nitrogen gas (purity > 99.999%, flow rate of 250 ml/min) was feeding into the reactor until the gas analyzer (Wuhan Cubic Optoelectronics Co., Ltd., China) monitored no impurity gases. When the reactor temperature was stable, the feeder was switched on and the biomass was fed into the reaction zone to start the pyrolysis. The volatiles successively passed through tar traps which were connected in series all filled with a mixture of HPLC-grade methanol and chloroform (20:80, vol, bought from Sinopharm chemical reagent Co., Ltd, Shanghai), and the tar was cooled and captured. The solvents volume of #1–#3 traps was 50, 50 and 30 ml, respectively. The #1 trap was cooled by ice salt water bath (0 °C), and another two traps were cooled by dry ice bath (–78.5 °C). The non-condensable gases were dried and entered the gas analyzer, then wholly collected by gas collector bag. When no non-condensable gases were determined by gas analyzer, the pyrolysis experiment finished. All of the pyrolysis time was no more than 20 min. To ensure the completion of pyrolysis experiment, each pyrolysis time was 20 min. Finally, the fresh mixture of methanol and chloroform solution was used to wash pipeline and traps after the experiment finished. The overall solutions were mixed well and weighed accurately, then collected in a brown bottle and stored in a freezer for further analysis.

After each pyrolysis experiment, the generated chars sample were carefully collected and accurately weighted. The chars yield was calculated by weight of the feeding sample. The tar yield was calculated by quantifying the tar concentration in above mixtures of which detailed quantified procedure was described in the following Section 2.5.1, and the gaseous yield was calculated by difference to acquire the distribution of pyrolysis products.

The composition of non-condensable gases (collected in the gas collector bag) were quantified by a dual-channel micro-GC system

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