



# Pyrolysis of rice straw with ammonium dihydrogen phosphate: Properties and gaseous potassium release characteristics during combustion of the products



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## HIGHLIGHTS

- The effect of  $\text{NH}_4\text{H}_2\text{PO}_4$  on rice straw (RS) carbonization is studied.
- The optimum carbonization operation of RS with  $\text{NH}_4\text{H}_2\text{PO}_4$  is determined.
- $\text{NH}_4\text{H}_2\text{PO}_4$  is very effective in inhibiting the gaseous potassium release.
- Potassium is retained in phosphorus compounds with high melting points.

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## ABSTRACT

The effect of ammonium dihydrogen phosphate ( $\text{NH}_4\text{H}_2\text{PO}_4$ ) on rice straw (RS) carbonization was evaluated at temperatures of 350–650 °C. The carbonized products of RS with  $\text{NH}_4\text{H}_2\text{PO}_4$  show higher solid and energy yields, but lower higher heating values than the carbonized RS at every carbonization temperature. The optimum carbonization operation of RS with  $\text{NH}_4\text{H}_2\text{PO}_4$  which has a higher energy yield at a lower solid volume may be determined between 350 and 450 °C, and RS with  $\text{NH}_4\text{H}_2\text{PO}_4$  carbonized at 450 °C presents better pore properties than carbonized RS. The carbonized products of RS with  $\text{NH}_4\text{H}_2\text{PO}_4$  all have lower gaseous potassium release ratios than those of RS carbonized at the same temperature at combustion temperatures of 700–1000 °C by retaining potassium in non-volatile phosphorus compounds with high melting points. It is an effective method for inhibiting the gaseous potassium release during combustion of the carbonized products.

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## 1. Introduction

Biomass regarded as a  $\text{CO}_2$ -neutral, renewable and sustainable energy source can be an alternative fuel to overcome the environmental effects and energy crisis in availability of conventional fossil fuels. However, biomass including a wide range of resources such as woody remnants, manure, agricultural leftovers, dedicated crops, herbaceous species, industrial and municipal solid wastes, algae, and biosolids only accounts for a minute proportion of energy generation in China (Balat et al., 2009; Fournel et al., 2015; Zhao and Liu, 2013). Biomass used as energy is limited by its bulky, fibrous, high moisture content and low energy density nature which will enhance the cost of transportation, multifarious equipment development and final energy consumption (van der Stelt et al., 2011). So co-firing of coal with biomass in existed

coal-based power plants has been widely applied and proved to be an effective approach to mitigate these aforementioned issues (Kabir and Kumar, 2012; Tamura et al., 2014; Steer et al., 2013). Nevertheless, the coarse biomass particles caused by the poor grindability of biomass may result in incomplete burn out, blockage/bridging to the feeding system, sedimentation and poor mixing (Abdullah and Wu, 2009), and the rapid burning of biomass at low temperatures due to its high volatile matter content can lead to segregation of the individual fuels in the blend during co-firing which will deteriorate the uniformity of the combustion process and cause operational problems (Haykiri-Acma et al., 2015). Co-firing of biomass with coal without any pretreatment is not promising and a method for biomass pretreatment prior to combustion allowing homogenization of the different biomass feedstocks into a coal-like biofuel to accommodate existing coal-fired systems is needed (Zhang et al., 2014).

Torrefaction and carbonization are slow pyrolysis processes for thermally biomass pretreatment which are usually applied at

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temperatures of 200–300 °C and 300–500 °C, respectively, in an inert or nitrogen atmosphere for several minutes to several hours. The grindability and energy density of torrefied and carbonized biomass are improved greatly due to the disruption of fibrous structure and release of volatile matter of biomass after the two methods (Chen et al., 2015, 2014; Luo et al., 2015). Du et al. (2014) evaluated the utility potential of pretreated biomass for pulverized coal injection in blast furnaces, the pretreatment temperatures of which were between 250 and 500 °C. It indicated that the obtained fuel properties such as fuel ratio, burnout, and ignition temperature, of biomass torrefied at 300 °C or carbonized between 400 and 500 °C, were between a high-volatile bituminous coal and a low-volatile one which could partially replace the coals consumed for pulverized coal injection and blend with coals. Sahu et al. (2010) investigated the combustion characteristics of blends of a coal with the chars of sawdust and rice husk pyrolyzed at 300 and 450 °C by thermogravimetric assessment. It depicted that the combustion characteristics of the coal/biomass-chars blends were improved according to the observation of lower activation energy and higher reactivity in major combustion zone. However, Park et al. (2012) examined the combustion profiles of the torrefied samples and the low-temperature carbonized samples of woody biomass blended with coal, and found that the DTG curves of the low-temperature carbonized samples were more similar to those shown by coal than those shown by the torrefied samples. It is necessary to pay attention to combustion control at the time of co-combustion of coal with torrefied biomass, because the torrefied samples show two DTG peaks. Besides, the devolatilization and burning characteristics of torrefied biomass are not so different from those of parent biomass because lignin and cellulose are decomposed at temperatures above 300 °C (Arias et al., 2008; Chouchene et al., 2010). Carbonization employs more severe conditions and consequently results in efficient break down of C–H and C–O bonds in lignin and cellulose which makes the carbonized products nearest to those of coals (Park et al., 2012; Haykiri-Acma et al., 2006). For these reasons, the carbonized product of biomass is more favorable in co-firing with coals.

However, biomass has a much higher content of potassium than most of the coals and the content is increased due to the dehydration and devolatilization reactions during the carbonization process. Some of the formed potassium compounds such as potassium salts and silicates with low melting points will melt and form viscous flow sintering and agglomeration on the surface of ash/char particles during co-firing with coal (Khan et al., 2009; Chaivatamaset et al., 2013). The volatilized potassium compounds mainly KCl in gaseous or aerosol phases will condense and deposit on heat transferring surfaces which will accelerate the corrosion (Enestam et al., 2013). Various approaches including co-combustion with other types of fuels and mixing with additives have been investigated and proved effective to reduce these potassium related operational problems (Kassman et al., 2013; Skoglund et al., 2013; Wang et al., 2014; Li et al., 2015). Based on the previous study, the addition of ammonium phosphates which will introduce phosphorus into the biomass are very effective in decreasing the gaseous potassium release ratio and can inhibit surface melting and sintering by forming potassium phosphate and potassium calcium phosphates with high melting points during the combustion of biomass. And the ashes containing phosphates can be reused as fertilizers which will benefit long-term sustainability. But unwanted NH<sub>3</sub> may be produced as a byproduct due to the ammonium group in the additives. It is known that ammonium dihydrogen phosphate will decompose and release NH<sub>3</sub> and H<sub>2</sub>O at temperatures above 200 °C (Su et al., 2014). Then biomass carbonized with ammonium dihydrogen phosphate at temperatures above 300 °C may be a promising method to only introduce phosphorus into the carbonized products during which the released

NH<sub>3</sub> can be absorbed together with the exhaust released from biomass carbonization.

To date, reports on the influence of additives on biomass carbonization and gaseous potassium release characteristics of the carbonized products are fairly limited. Rice straw has a high potassium content and is widely used for biomass molding fuel and power generation in north China. In this study, various fuel properties of the products of rice straw carbonized with ammonium dihydrogen phosphate at temperatures of 350–650 °C were investigated. Furthermore, gaseous potassium release characteristics during combustion of the carbonized products were also examined. The results from this study will contribute to optimizing the carbonization process of rice straw with ammonium dihydrogen phosphate and evaluating the potential potassium related operational problems of using the carbonized products as alternative to co-fire with coals.

## 2. Methods

### 2.1. Materials and preparation

Rice straw (RS) collected from Dezhou, Shandong Province was used in this study. The received rice straw was ground and sieved with a sieve of 80 mesh (i.e. 180 μm). The basic properties of rice straw and the carbonized products such as proximate, ultimate and calorific analyses were measured based on air dried basis. The proximate analysis was in accordance with the standard procedure of Chinese GB/T 28731–2012 codes. The ultimate analysis was carried out using an elemental analyzer (LecoTruSpec CHN) and sulfur analyzer (Leco S144DR). The potassium content in the rice straw and carbonized products was measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Thermo Fisher Scientific, IRIS Advantage). The higher heating values (HHVs) of the raw rice straw and carbonized products were measured by a bomb calorimeter (CKIC 5E-AC8018) and all reported as air dried basis. Ammonium dihydrogen phosphate (NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>, ADP) (Kemiou Chemical Reagent Co.) which was analytically pure was ground and sieved with a sieve of 200 mesh (i.e. 75 μm) to make the particles be easier to mix with rice straw. The potassium content of raw RS is 2.09% (wt/wt), and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> was mechanically blended with a given weight of raw RS with a molar ratio PO<sub>4</sub><sup>3-</sup> to K 1:1 i.e. NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> content in the mixture was 5.8% (wt/wt). The mixture was stirred for 1 h by a motor stirrer to ensure the homogeneous mixture. The ash content of the rice straw was analyzed by X-ray fluorescence spectrometer (XRF) (Rigaku Co., ZSX Primus II). According to the XRF results, SiO<sub>2</sub> and K<sub>2</sub>O are the main compositions with contents of 58.81% and 20.45% (wt/wt) in the ash. The other compositions detected are Na<sub>2</sub>O, MgO, Al<sub>2</sub>O<sub>3</sub>, P<sub>2</sub>O<sub>5</sub>, CaO and Fe<sub>2</sub>O<sub>3</sub> with contents of 0.74%, 2.74%, 0.34%, 2.08%, 3.89% and 0.52%, respectively.

### 2.2. Reaction system

The carbonization experiment was conducted on a common horizontal pyrolyzer and the schematic is presented in [Supplementary data 1](#). The experimental setup was made up of a gas feeding unit, a carbonization unit and a gas treatment unit. The steel cylinder labeled with nitrogen was used to supply high purity nitrogen (>99.99%) for providing inert atmospheres. The volumetric flow rate of nitrogen was controlled by the rotameter. The carbonization unit comprised a corundum tube with sealing flanges and an electrical furnace. The inner diameter and length of the tube were 68 and 600 mm respectively. The flanges of both ends were welded with stainless pipes connected with silicon tubes to transport the nitrogen and exhaust, the inner diameter of which was 8 mm.

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