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RESEARCH PAPER

Effect of potassium on pyrolysis of rice husk and its components

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Abstract: Different rice husk samples and their components (cellulose, hemicellulose and lignin) were investigated with emphasis on the influence of potassium on their pyrolysis behaviors by using thermogravimetric (TG) analysis. The results indicate that the maximum weight loss rate of cellulose decreases with the addition of KCl. However, no significant differences are observed for the pyrolysis behavior of hemicellulose and lignin. The TG/DTG curve of a model rice husk (a mixture of cellulose, hemicellulose and lignin) could be obtained by superposition of that for each component. However, during pyrolysis the raw stable structure of basic components in the rice husk results in a change from a sharp peak for the model rice husk to a shoulder peak for the AW rice husk (pretreated with HCl to remove K and the other mineral matters) at around 300°C. In addition, the effect of KCl addition on pyrolysis of the AW rice husks was also studied. The results show that potassium has a remarkable catalytic effect on pyrolysis of the rice husk samples. The pyrolysis characteristics vary depending on the addition methods of KCl. While char yields decrease with the addition of KCl using mechanical method (except for the cellulose), the char yield and the maximum weight loss rate of impregnated AW rice husk increase gradually with the increase of KCl content.

Key words: TG; rice husk; mechanical mixing; impregnation; KCl

Biomasses are commonly accepted as one of the sustainable and renewable energy resources. They could be converted to gas, liquid and solid products through various thermo-chemical technologies such as gasification and pyrolysis[1,2]. The commercial utilization of biomass energy is an alternative to fossil energy to certain extent. In general, biomasses vary in its composition, depending on the species. The main components of biomass are cellulose (40%–50%), hemicellulose (15%–20%), lignin (20%–30%), and small amount of mineral matters, such as K, Na, Ca and Mg, based on the dry base[3]. The product yield and distributions are affected by the presence of mineral matters, especially K, during biomass pyrolysis[4,5]. There are various forms of K existence during biomass growth process, and this complicates its effect on the thermo-chemical conversion of biomass.

K and other metallic elements exist in biomass in various forms, including ion state, interacting with organic matrix, and mineral particles[6]. Water-soluble K mainly presents in biomass in ion bonded state and minerals, while the K on the organic oxygen-containing functional groups is not soluble in water. Moreover, the form of K may change during pyrolysis of biomass, and K on the original binding sites of biomass may be deposited as fine potassium salt (mainly KCl and K_2CO_3) particles, or mixed with product char, or dispersed on char surface. Knudsen et al[7] reported that most K was released from the original binding sites when the pyrolysis temperature of straw was above 700°C. Some of the potassium was transformed from the original binding sites to gas phase, and the remaining presented in product char in the forms of KCl and K_2CO_3, potassium silicates, or being bonded to organic matrix.

Inherent K in biomass has catalytic effect on its thermo-chemical conversion. Additionally, externally added K might also act as catalyst during biomass pyrolysis. The intrinsic K could restrain the formation of volatile, and lower the initial pyrolysis temperature and the weight loss rate[8–10]. Nowakowski et al[6] reported that K could reduce the average apparent activation energy for willow coppice pyrolysis by up to 50 kJ/mol, and enhance the yields of char and CH_4. In the case of K in a synthetic biomass sample, the formation of levoglucosan was promoted during pyrolysis of cellulose. It is believed that external or added K promoted the formation of

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low molecular weight products and char during pyrolysis of poplar wood, and the pyrolysis peak was shifted towards the lower temperature range[11]. However, addition of excessive K_2CO_3 could promote pyrolysis of peanut shell at higher temperature, and hinder the volatile release[12]. The correlation between inherent and added K has not been understood well. And their effects on the pyrolysis of biomass and its three components (cellulose, hemicellulose and lignin) need to be further studied.

Cellulose, hemicellulose, lignin, rice husk, model rice husk (mixture of cellulose, hemicellulose and lignin), and AW rice husk (pretreated with HCl to remove K and the other mineral matters) were selected as the samples in this study. The effect of K on the pyrolysis characteristics of the samples were investigated by thermogravimetric (TG) analysis. The addition of KCl by mechanical mixing and impregnation method were also explored. The results will provide a better understanding of the effect of K on the biomass pyrolysis for desired products.

1 Experimental

1.1 Biomass samples

The rice husk sample, used as the raw biomass materials, was ground and sieved. The fraction 0.12–0.15 mm (120–100 mesh) was dried at 105°C for 4 h before use. The ultimate, proximate and chemical composition analyses of rice husk are listed in Table 1 and Table 2, respectively.

The commercial cellulose, hemicellulose and lignin (alkaline) were dried at 105°C for 4 h before the experiment. Xylan obtained from bagasse was chosen as the substitute for hemicellulose. The model rice husk with a certain amount of basic biomass components: cellulose (40.2%), hemicellulose (24.3%), lignin (18.1%) was obtained by mechanical mixing for 12 h. The sample was then dried at 105°C for 24 h before use.

1.2 Biomass pretreatment

Portion of the rice husk sample was firstly treated with 7% HCl (mass ratio of biomass to HCl solution was 1:50) for 2 h and filtered, while magnetic stirring was kept. The filter cake, treated rice husk using HCl, was washed with ultrapure water to ensure the removal of trace HCl. Finally, it was dried at 105°C for 24 h before use, and labeled as AW rice husk.

1.3 Addition of KCl

1.3.1 Mechanical mixing of biomass samples

KCl was added to the tested samples using mechanically mixing method for 12 h. The mass ratio of K to the samples was 1%, 3%, and 5%, respectively. Then the mixed samples were dried at 105°C for 24 h before use.

1.3.2 Impregnation of AW rice husk

About 3 g AW rice husk was immersed in 150 mL of KCl solution of 1%, 5%, and 10%, respectively. The magnetic stirring was maintained for 10 h during the impregnation processing. The impregnated samples were then filtrated, and dried at 105°C in air for 24 h before use.

1.4 Thermogravimetric (TG) tests

TG analysis was carried out using a Q50 instrument (TA Instrument, USA). Typically, a 10 mg sample was treated in 60 mL/min N_2 for 10 min, and then heated from room temperature to 900°C at 20 K/min.

1.5 Analysis method

The content of K in different biomass samples was measured by atom absorption spectrometry (AAS) using WFX-120 Elemental analyzer (Beijing Beifen-Ruili analytical instrument, China). 0.2 g biomass sample was wet-digested with 10 mL HNO_3 (A.R.) and 4 mL H_2O_2 (A.R.) before determination.

Table 1 Ultimate and proximate analyses of rice husk

Sample	Ultimate analysis w_d/%				Proximate analysis w_d/%			
	C	H	N	O*	*M*	*V*	*A*	FC*
Rice husk	39.82	5.10	1.09	53.87	4.7	69.3	15.8	10.2

*: by difference

Table 2 Chemical composition analysis of rice husk

Sample	Composition* w_d/%			
	cellulose	hemicellulose	lignin	extractives
Rice husk	40.2	24.3	18.1	17.2

*: dry ash free basis