Applied Energy 178 (2016) 346–352

Contents lists available at ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy

The effect of sodium chloride on the pyrolysis of rice husk

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HIGHLIGHTS

- Yield of bio-oil was increased with the presence of NaCl catalyst during rice husk pyrolysis.
- Quality of bio-oils from catalytic pyrolysis improved with NaCl catalyst addition.
- CO content decreased and CO_2 and H_2 increased using NaCl catalyst.

ARTICLE INFO

Article history:
Received 28 December 2015
Received in revised form 2 June 2016
Accepted 17 June 2016

Keywords:
Rice husk
NaCl catalyst
Catalytic pyrolysis
Catalyst-to-biomass ratio
Bio-oil

ABSTRACT

Pyrolysis of rice husk with or without catalyst was investigated in a fixed bed reactor to determine the effect of sodium chloride (NaCl) catalyst on the yields of three products, the properties of the bio-oils and the gas composition. At the optimum pyrolysis conditions, the bio-oil yield obtained in non-catalytic pyrolysis process was 53.81 wt.%, while that of catalytic pyrolysis maximumly increased to 57.61 wt.% with 3 wt.% NaCl catalyst. The composition of bio-oils was analyzed by gas chromatography/-mass spectrometry (GC/MS) and the results indicated that the catalyst would pierce through the rice husk textures to act on cellulose, hemicellulose and lignin and change the pyrolysis reaction pathways, which decreased the percentage of organic acids, esters, ketones, guaiacols and aldehydes, but increased the percentage of alcohols, phenols, furans and anhydrosugars, along with getting more small molecular compounds. Quality of the bio-oils from catalytic pyrolysis was improved, which carried higher heating value and lower acid value. The maximum heating value and the minimum acid value of bio-oils were 27.09 MJ/kg and 68.33 mg KOH g^{-1}, obtained with 3 wt.% and 4 wt.% NaCl catalyst, respectively, which were 5.12% higher and 14.83% lower than that of non-catalytic pyrolysis. The gas chromatography (GC) analysis of non-condensable gas showed that CO content decreased and CO_2 and H_2 increased with NaCl catalyst addition, obviously.

1. Introduction

The demand of energy and its resource is increasing continuously due to the rapid outgrowth of population and economic developments [1]. As the widely used energy sources are still limited to the conventional fossils such as coal, petroleum and natural gas, which are at the verge of getting extinct [2]. Biomass is an abundant and renewable energy source derived from all organic materials produced by human and natural activities [3]. Biomass can be considered as one of the promising environment friendly renewable energy options and has attracted more and more interests [4]. Rice husk from the agricultural industries is an abundant biomass resource in China that has typically been treated using traditional methods such as composting and incineration. However, they are not suitable to process this solid waste as rice husk contains small concentrations of nitrogen for composting and a considerable amount of solid grains that would generate smoke into the environment during incineration [5]. As the rich in volatiles and combustible ingredients, the rice husk can be employed as a renewable energy source. How to reuse and recycle this valuable biomass resource is a very urgent significant, yet difficult job [6].

Biomass can be converted into fuel products through different thermochemical processes, among which pyrolysis is considered as a prospective and effective technology to produce valuable bio-oils, char and gaseous [7–9]. Especially, the bio-oils obtained from pyrolysis processes are attractive and considered to be a very promising biofuel as their high energy density and convenience in usage, storage and transport [10]. Bio-oils in general are dark brown, free-flowing organic liquids that cannot be used directly as a regular fuel due to their high oxygen content, high viscosity, high corrosiveness, relative instability and complex chemical com-

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http://dx.doi.org/10.1016/j.apenergy.2016.06.082
0306-2619/

position, and need to upgrade by complicated process [11]. It is desirable and necessary to improve the quality of bio-oil toward properties similar to those of hydrocarbon fuel by certain upgrading techniques [12]. Several methods have already been examined for upgrading the bio-oil quality, namely, catalytic cracking of pyrolysis vapors, hydrodeoxygenation, extracting chemicals, and esterification etc. [13]. Among these methods, catalytic pyrolysis of biomass has been receiving great attention in recent years due to its obvious advantages of simplifying process and improving the quality of bio-oil, which uses a catalyst to directly penetrate into biomass textures and enhance reactions that include cracking, decarbonylation, decarboxylation [14]. In this process, the products depend on the characteristics of the catalyst used. Choosing a suitable catalyst, not only is selective enough to control the distribution of pyrolysis products, increase production of certain target products, can also improve the quality of bio-oil.

Recent articles have researched many kinds of catalysts for pyrolysis of lignocellulosic biomass. Auta [15] studied fixed-bed catalytic and non-catalytic empty fruit bunch biomass pyrolysis. It was observed that the quantity and quality of bio-oils can be improved using $Ca(OH)_2$. Guo [16] concluded that the maximum mass loss rate decreased with increasing amount of NaOH and Na_2CO_3 additives in the pyrolysis process of alkali lignin. Xu [17] investigated fast pyrolysis of pine sawdust for bio-oil over MoNi/γ-Al_2O_3 catalyst under mild conditions. The results showed that this catalyst could increase the pH value, gross calorific value and hydrogen content. However, studies on catalytic pyrolysis of rice husk are quite limited. In an earlier research, Williams [18] studied the catalytic pyrolysis of rice husk with zeolite ZSM-5 in a fluidised reactor. The results indicated that in the presence of the catalyst the yield of bio-oil was reduced, but the catalyzed bio-oils were increased in single ring. In a recent work, Bakar [19] also tested commercial zeolite and zeolite-like material in the pyrolysis of rice husk. It was observed that the catalysts increased the heating value and water content of the bio-oils, whilst viscosity, density and acid number were decreased. Jeon [20] studied catalytic pyrolysis of waste rice husk over mesoporous materials, and the yield of catalytic pyrolysis bio-oil was decreased, but levoglucosan was completely decomposed without being detected in the bio-oils, and the amount of aromatics increased remarkably. These studies always discussed catalytic pyrolysis of rice husk with molecular sieve based catalysts and commercial catalysts, and extensive research has been conducted to understand the effect of these catalysts on the thermal decomposition of biomass for elucidating reaction mechanisms [21–23]. However, inorganic minerals, mainly alkali and alkali earth metals, are only known to influence pyrolysis behaviors and affect pyrolysis products yields, significantly [24–26]. Studies on the characteristics of products and reaction mechanisms of catalytic pyrolysis with inorganic minerals are less, especially, with regard to catalytic pyrolysis of rice husk. This is the focus of our research.

Among the alkali and alkali earth metals, sodium chloride (NaCl) catalyst is expected to be mild and inexpensive. In this paper, rice husk and NaCl were chosen respectively as the feedstock and catalyst. Experiments of the rice husk pyrolysis with and without NaCl were performed in a fixed-bed reactor. The effect of NaCl catalyst on the yields of three products, properties of the bio-oils and gas composition were investigated and discussed.

2. Experimental

2.1. Material and catalyst

The sample rice husk used for the experiments was taken from the countryside near Huaqiao University in Xiamen, China. The rice husk was dried in an electrical oven for 24 h at 105 °C to ensure the reduction of free moisture. Before pyrolysis, the rice husk was passed through in high speed rotary cutting mill and then sieved to obtain the maximum particle size of 0.16 mm. Table 1 shows the characterization data for the rice husk sample used. The proximate analysis was performed to measure the moisture content, volatile matter and ash content of rice husk following the National Standards of China GB/T 28731-2012 (similar to CEN/TS 14774-3:2004, CEN/TS 14775:2004 and CEN/TS 15148:2005). The analysis results show that rice husk has a high volatile matter and high ash content. The ultimate analysis of rice husk, which mainly consists of Carbon, Hydrogen, Nitrogen and Oxygen, was carried out by using an Elemental CHNS/O 2400 analyzer. The composition analysis of rice husk was determined by the Van Soest method [27,28], which revealed that the rice husk is high in cellulose and lignin content. The heating value of rice husk and bio-oil was measured by ZDHW-2A automatic bomb calorimeter.

NaCl catalyst used in the experiments was produced by the Xilong chemical company, China. The purity was approximately 99.5% and the particle size 0.1–0.2 mm. Some other main impurity particles were K (<0.02 wt.%) and bromide(<0.01 wt.%). Prior to use, the catalyst was calcined at 400 °C for 3.5 h to eliminate the water and kept in a desiccator for the experiments.

2.2. Pyrolysis

The pyrolysis experiments were performed by mixing the catalyst with rice husk at in-bed mode in the fixed-bed reactor. The schematic diagram of the experimental fixed-bed pyrolyzer is shown in Fig. 1. The experiments were conducted by mixing 16 g rice husk with various ratios of the catalyst (1, 2, 3, 4, 5 wt.% of rice husk) at the optimum experimental conditions, which determined in a previous study were a final pyrolysis temperature of 550 °C, a heating rate of 20 °C/min, a sweeping gas (N_2) flow rate of 300 mL/min and a mean particle size of 0.16 mm. The pyrolysis process resulted in bio-oil, char and gas products. The flow of gas released was measured using wet gas flowmeter for the duration of experiments. The mass of gas product was calculated by analyzing the total volume and average relative molecular mass, combined with the molar volume of the gas. The char remained in the reactor was quantified by weight. The liquid product was collected from the cold trap and a series of condensers and recovered by washing with acetone. The bio-oil yield was calculated from overall material balance. In this study, all pyrolysis products yields and properties were expressed a dry ash-free(daf) basis and the mean values of at least three experiments were given within the experimental error of less than ±2%.

2.3. Analysis of pyrolysis products

The non-condensable gases produced from non-catalytic and catalytic pyrolysis experiments were collected in a gas bag and

Table 1
Characterization of rice husk.

Proximate analysis[a]	Wt.%	Ultimate analysis[b]	Wt.%	Composition analysis[c]	Wt.%
Moisture	5.62	Carbon	43.39	Cellulose	34.56
Volatile matter	62.61	Hydrogen	6.56	Hemicellulose	23.54
Ash	17.82	Nitrogen	1.06	Lignin	24.53
Fixed carbon	13.95	Oxygen	48.34	Extractives	11.69
Heating value (MJ/kg)		16.68		Acid-insoluble ash	5.68

[a] Dry basis.
[b] Dry and ash-free.
[c] Dry, ash and extractives free.