



Pressurized pyrolysis of rice husk in an inert gas sweeping fixed-bed reactor with a focus on bio-oil deoxygenation



Yangyang Qian, Jie Zhang, Jie Wang*

Department of Chemical Engineering for Energy, Key Laboratory of Coal Gasification and Energy Chemical Engineering of Ministry of Education, East China University of Science and Technology, 130#, Meilong Road, Shanghai 200237, PR China

HIGHLIGHTS

- Pressurized pyrolysis of rice husk was conducted in a fixed-bed reactor.
- Pressure accelerated the dehydration and decarboxylation of bio-oil.
- The bio-oil produced under pressure had less oxygen and higher calorific value.
- Pressure increased the yields of acetic acid, PCX and guaiacols.

ARTICLE INFO

Article history:

Received 26 August 2014
Received in revised form 1 October 2014
Accepted 4 October 2014

Keywords:

Rice husk
Pyrolysis
Pressure
Bio-oil
Deoxygenation

ABSTRACT

The pyrolysis of rice husk was conducted in a fixed-bed reactor with a sweeping nitrogen gas to investigate the effects of pressure on the pyrolytic behaviors. The release rates of main gases during the pyrolysis, the distributions of four products (char, bio-oil, water and gas), the elemental compositions of char, bio-oil and gas, and the typical compounds in bio-oil were determined. It was found that the elevation of pressure from 0.1 MPa to 5.0 MPa facilitated the dehydration and decarboxylation of bio-oil, and the bio-oils obtained under the elevated pressures had significantly less oxygen and higher calorific value than those obtained under atmospheric pressure. The former bio-oils embraced more acetic acid, phenols and guaiacols. The elevation of pressure increased the formation of CH₄ partially via the gas-phase reactions. An attempt is made in this study to clarify “the pure pressure effect” and “the combined effect with residence time”.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Biomass has been receiving considerable interest as a renewable and carbon-neutral energy resource in recent years due to the worldwide increased concerns on the shortage of fossil fuels, climate change and environmental pollution. Rice husk is a byproduct in mill factories with the productivity of about twenty percent from rice grain. It is available as a biomass feedstock in many agrarian countries primarily in Asia. The annual output of rice husk in China is estimated to be about 70 million metric tons and accounts for about half of the world output (Yoon et al., 2012). Rice husk is concentrated with lignocellulosic components (i.e., cellulose, hemicellulose and lignin) with a half as much calorific value as that of coal, but it has a very low bulk density so that its distant transport is economically limited. In China, rice husk is

mainly used in burning for rural households and small boilers in local areas. Such energetic uses of rice husk has the demerit of low efficiency and high smoke emission. Pyrolysis offers a promising way to convert rice husk to more energy-intensive and value-added products such as bio-oil and bio-char.

Biomass pyrolysis has been investigated extensively from varying viewpoints. Numerous recent studies have focused on the bio-oil production by fast pyrolysis of various biomass species, such as cassava stalk and rhizome (Pattiya, 2011), forestry residues (Amutio et al., 2013), jute stick (Asadullah et al., 2008), maize stalk (Zheng, 2008), mallee leaves (He et al., 2012), microalgae remnants (Wang et al., 2013), *Miscanthus sinensis* (Heo et al., 2010), red oak (Ellens and Brown, 2012) and waste plywood (Jung et al., 2012). The fluidized-bed, conical spouted bed and fall free reactors are employed for fast pyrolysis. Rapid heating rate with short vapor residence time is favorable to maximize the yield of bio-oil as a consequence of the suppressed secondary cracking reactions (Bridgwater, 1999). Traditionally slow pyrolysis is applied for the production of charcoal and gas. However, the slow pyrolysis with

* Corresponding author. Tel./fax: +86 21 64252853.

E-mail address: jwang2006@ecust.edu.cn (J. Wang).

gas sweeping over the heated biomass sample permits the volatile matter to leave promptly from the hot zone and can consequently avoid its violent cracking to gases. Gercel (2002) used a fixed-bed reactor to pyrolyze a sunflower-pressed bagasse with the heating rate of 5 °C/min in a flow of nitrogen. A bio-oil yield of 52% was obtained at 550 °C. The average compositional formula of bio-oil was $\text{CH}_{1.68}\text{O}_{0.165}\text{N}_{0.059}$. Wang et al. (2009) carried out a similar slow pyrolysis of pine wood in a stream of argon, and observed that the compounds in the bio-oil reflected the initial or mild degradation from the lignocellulosic components. The slow pyrolysis of a microalgae (*Tetraselmis chui*) by passing helium through the packed biomass sample (Grierson et al., 2011) demonstrated that the bio-oil consisted of a wide variety of compounds including fatty acids, alkanes, alkenes, amides, aldehydes, terpenes, phenols, etc.

The biomass pyrolysis by any measures to mitigate the volatile matter cracking is inclined to achieve a good harvest of bio-oil. In general, however, the resultant bio-oil contains abundant oxygen. This is deemed to be responsible for its drawback of low heating value, lipophilicity and instability, restricting its application. Several approaches have hence emerged to upgrade the bio-oil before, during and after pyrolysis (Stefanidis et al., 2011; Veses et al., 2014). A common tactics adopted in most approaches is to eliminate the oxygen from bio-oil. The adjustment of operating parameters such as temperature, heating rate and atmosphere during biomass pyrolysis is known as a straightforward way to change the pyrolysis characteristics and the formation of bio-oil (Ben and Ragauskas, 2013; Chhiti et al., 2012; Zhang et al., 2011). However, it can be often difficult to determine an optimal balance of the yield of bio-oil against the quality.

There are a number of publications pertaining to the pyrolysis of rice husk. Mansaray and Ghaly (1999) studied the decomposition of four rice husks using thermogravimetric analysis (TGA). Worasuwannarak et al. (2007) investigated the pyrolysis behaviors of rice husk together with rice straw and corncob by means of TG-MS. Zheng (2007) reported the fast pyrolysis of rice husk on a fluidized-bed reactor in which the highest bio-oil yield of 56% (including water) was obtained at 465 °C. Tsaia et al. (2007) used a fixed-bed reactor to pyrolyze rice husk with a rapid heating rate (500–800 °C/min) and obtained a maximal bio-oil yield of 40% (including water). Their GC-MS analysis showed that the bio-oil consisted of copious oxygen-containing compounds. Chen et al. (2011) characterized the bio-oil produced from the pyrolysis of rice husk in a fluidized-bed reactor. Nevertheless, the average bio-oil yield of 41.7% obtained in their experiment at 500 °C appeared to be lower than normal, whereas the average water content of 41.5% in the bio-oil appeared to be higher. Zhou et al. (2013) investigated the catalytic pyrolysis of rice husk mixed with zinc oxide in a fixed-bed reactor towards the bio-oil production, and found that addition of the catalyst reduced the yield of bio-oil and changed its rheological properties. Alvarez et al. (2014) performed the pyrolysis of rice husk using a conical spouted bed reactor. The bio-oil yields (excluding water) of 44–47% and the water yields of around 23% were obtained at 450–600 °C. The yields of acetic acid ranged in 2.35–3.16%.

In this work, we examine the pyrolysis characteristics of rice husk in a fixed-bed reactor purged with a pressurized nitrogen gas. To the best of our knowledge, there are few studies in the literature concerning the influence of pressure on biomass pyrolysis. Whitty et al. (2008) investigated the influence of pressure on black liquor using a single-particle reactor and a grid heater. Their interest was centered on the char and gas production. Mercader et al. (2010) proposed the high-pressure thermal treatment for upgrading pyrolytic oil. They found that the treatment under a condition of 300–340 °C and 20 MPa was effective to liberate gas (mainly CO_2) and water from the pyrolytic oil. In the present study, we have found that the pressurized pyrolysis has a similar effect on

preferential removal of oxygen from bio-oil by the facilitated dehydration and decarboxylation.

2. Experimental

2.1. Rice husk sample

The rice husk used in this work was kindly supplied by a mill factory in Zhejiang province, China. The sample was ground and sieved to the particle size of about 0.15–0.45 mm. The proximate analysis showed that the dried rice husk had 1.55% moisture, 72.58% volatile matter, 16.01% fixed carbon and 9.86% ash. The ultimate analysis showed that the rice husk (daf. basis) had 51.20% carbon, 6.17% hydrogen, 42.16% oxygen (by difference), 0.36% nitrogen and 0.10% sulfur. The componential analysis showed that the rice husk (dry basis) contained 42.94% cellulose, 14.85% hemicellulose, 25.79% lignin and 7.60% neutral detergent solute. Cellulose, lignin and hemicellulose comprised more than 92% of the organic entity. The content of either cellulose or lignin in the rice husk was higher than that reported by Li et al. (2012) and Chen et al. (2011) but close to those reported by Bakar and Titiloye (2013).

2.2. Pyrolysis apparatus and procedures

Pyrolysis was carried out in a vertical tubular fixed-bed reactor made of inconel steel. The schematic diagram of the apparatus was illustrated elsewhere (Zhang et al., 2014). In each run, a 4 g sample of rice husk was wrapped by a stainless steel wire mesh and then placed on the ceramic filler in the flat-temperature zone of the reactor. The dehumidified nitrogen gas was flowed from the inlet at the bottom of reactor to the outlet at the top, sweeping through the biomass sample. The gas flow rates were controlled by a mass flow meter from 10 mL/min to 500 mL/min. The gas pressures were controlled by a counterbalance valve from 0.1 MPa to 5.0 MPa. After no gas leakage was guaranteed and the air enclosed inside the reactor was driven out, the reactor was electrically heated at a predetermined heating rate of 15 °C/min from room temperature to 700 °C for a holding time of 60 min. In order to detect the pyrolysis temperature, a thermocouple was inserted into the reactor and its tip was forced to tightly contact the sample mesh. The volatile matter was purged out and condensed in a stainless steel trap immersed in the cooled salt water which maintained the temperatures from –12 °C to –6 °C during the experiment. The tube lines connecting the reactor to the trap was heated at 280 °C with a heating tape to prevent the condensation of the volatile matter. The incondensable gases were collected in the gas bags at a temperature interval of 50 °C in the heat-up stage and at a time interval of 10 min in the temperature-holding stage. The flow rate of total gas including the swept gas and gaseous product was measured by another mass flow meter after depressurization. Char product was recovered after the reactor was dismantled.

2.3. Analytical methods

The liquid yield was determined by weighing the trap before and after experiment. The liquid product was then carefully washed out with acetone (AR grade) into a glass bottle, which was then sealed up for later analyses of water and organic compounds in it. The water content in the liquid product was determined using a Coulometry trace moisture analyzer (Mettler Toledo, C20). The compounds in the liquid product were characterized by gas chromatography mass spectrometry (GC-MS, PerkinElmer clams 500). The quantitative determination of typical compounds was carried out on a GC-FID analyzer (Haixin

Download English Version:

<https://daneshyari.com/en/article/7075960>

Download Persian Version:

<https://daneshyari.com/article/7075960>

[Daneshyari.com](https://daneshyari.com)