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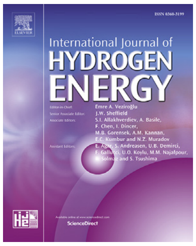

Assessment of sugarcane bagasse gasification in supercritical water for hydrogen production

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ABSTRACT

Sugarcane bagasse is one of the major resources of agricultural biomass waste in the world. In this work, supercritical water gasification characteristics of sugarcane bagasse were investigated. The effect of temperature (600–750 °C), concentration (3–12 wt%), residence time (5–20 min) and catalysts (Raney-Ni, K_2CO_3 and Na_2CO_3) on bagasse gasification were studied. A kinetic study on the non-catalytic and Na_2CO_3 catalytic bagasse gasification was conducted to describe the kinetic information of the bagasse gasification reaction. The results showed that a higher reaction temperature, a lower bagasse concentration and a longer residence time could favor the gasification of bagasse, leading to a higher hydrogen yield. Bagasse was nearly completely gasified at 750 °C without using any catalyst and the carbon gasification efficiency could reach up to 96.28%. The addition of employed catalysts remarkably promoted the bagasse gasification reactivity. The maximum hydrogen yield (35.3 mol/kg) was achieved at 650 °C with the Na_2CO_3 loading of 20 wt%. The experimental data fitted well with a homogeneous model based on a Pseudo-first-order reaction hypothesis. The kinetic study showed that Na_2CO_3 catalyst could lower the activation energy E_a of bagasse gasification from 117.88 kJ/mol to 78.25 kJ/mol.

Introduction

With the deteriorating of global warming and fossil fuel depletion issues, the environmental pollution and energy crisis are expected to be the two main challenges for human being in the long-term future. Since bio-waste is a renewable and carbon neutral energy resource, conversion of bio-waste into hydrogen and other fuels has attracted considerable attention [1,2]. Sugarcane bagasse (SB) is a kind of fibrous residue produced after extracting the juice of sugarcane. It is an abundant source of lignocellulose, and has become one of the major resources of agricultural bio-waste in the world [3]. Bagasse generated from the sugarcane diffusion and milling processes generally contains 44–53% moisture, 1–2% soluble solids, 1–5% insoluble solids (ash) and the remainder lignocellulosic fiber [4]. Reports on SB fiber composition in the literatures vary with cellulose typically 45–55%, hemicellulose 20–25% and lignin 18–24% on a dry basis [5]. The Australia sugarcane industry is planning to investigate the conversion of the surplus bagasse into energy fuels and more commercially valuable chemical sources.

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Among the energy fuels, hydrogen has attracted increasing attention due to its unique nature and it has been thought to play an essential role in the future energy sectors. Hydrogen can be produced from many different energy sources and by various technologies [6]. Supercritical water gasification (SCWG) is a novel and effective method to convert bio-waste into hydrogen, featured by its high reaction efficiency and H_2 selectivity [7,8]. Hosseini et al. reported that SCWG technology is the most cost-effective thermochemical process to convert bio-waste into hydrogen [9]. A variety of bio-wastes have been successfully gasified in supercritical water, including sewage sludge [10,11], chicken manure [12], industrial organic waste [13] and black liquor [14,15], etc. The hydrogen yield of different biomass wastes varied based on their gasification characteristics. Besides, the high moisture content bagasse could be gasified directly in supercritical water without prior drying process [16].

During the past two decades, excellent work has been done on SB gasification in supercritical water. The previous investigations mainly focused on the influence of operating conditions and catalysts on gasification efficiency. For example, Osada et al. [17] studied the gasification of SB with the addition of Ru/C and Ru/TiO_2 catalysts in supercritical water. SB was completely gasified to H_2, CH_4 and CO_2 over Ru/C and Ru/TiO_2 catalysts at 673 K. Barati et al. [18] investigated the use of unpromoted and zinc promoted $Ru/\gamma\text{-}Al_2O_3$ nanocatalysts on hydrogen yield from SB. It was shown that the maximum hydrogen yield was 15.6 mol/kg. M Sheikhdavoodi et al. [19] studied the SCWG of SB in a batch reactor. The maximum hydrogen yield was achieved at 800 °C in the presence of KOH. M Rashidi et al. [20] studied the SCWG of SB in the presence of Ni/CNTs nanocatalyst. Results showed that 20 wt% Nickel over CNTs (20%-Ni/CNTs) has the best performance on the SCWG of bagasse.

However, few studies on SCWG of SB have been reported, especially on the kinetics analysis, which is important for reactor design. In this work, the SCWG characteristics of sugarcane bagasse were investigated. Firstly, pyrolysis of SB sample under steam atmosphere was investigated by a thermogravimetric analyzer to study the pyrolysis characteristic of SB. Then, the effects of temperature, bagasse concentration, reaction time and catalysts on gasification were studied. At last, a simplified kinetics study on the non-catalytic and Na_2CO_3 catalytic bagasse gasification reaction was done by the assumption of Pseudo-first-order reaction, the activation energy of SB gasification with and without catalyst in supercritical water was obtained.

Experimental section

Material analysis

Sugarcane bagasse was obtained from Mulgrave sugar mill, Queensland, Australia. Bagasse was ground for reducing particle size by a micropipette grinder and sieved into 100 meshes by a screen mesh. Before being analyzed, SB sample was dried at 105 °C for 12 h in an oven. The proximate analysis, ultimate analysis and chemical composition results of SB were listed in Table 1. The proximate analysis and chemical composition results were obtained from the laboratory in Coal Geological Bureau in Shaanxi province.

The anhydrous K_2CO_3 and Na_2CO_3 were purchased from Tianjin Tianli Chemical Company, and the Raney-Ni was purchased from Dalian Tongyong Chemical Company. The main metal element of Raney-Ni catalyst is listed as follows: Al (9.47%), Ni (82.68%) and Fe (7.86%).

Besides, the pyrolysis characteristic of SB under steam atmosphere was studied. The SB sample was heated up to 800 °C at a heating rate of 10 °C/min and then held for 10 min, the rate of water vapor flow was 20 mL/min. The thermogravimetric (TG) curve was obtained directly from the experiment which showed the weight loss of sample with temperature. The differential thermogravimetric (DTG) curve was obtained from the TG curve by differential calculation. The DTG curve showed the decomposition rate of SB during the pyrolysis process. The peaks of DTG curve indicated that the weight loss of SB reached a maximum rate at 288 °C and 338 °C as shown in Fig. 1. This phenomenon is well known for lignocellulosic biomass feedstock, where those two peaks are mainly attributed to hemicellulose and cellulose decomposition. Yang et al. [21] studied the pyrolysis behavior of three main components (hemicellulose, cellulose and lignin) of biomass and found that the weight loss of hemicellulose mainly happened at 220–315 °C and that of cellulose at 315–400 °C. As for a specific biomass, the pyrolysis characteristic is highly influenced by the presence of inorganic salt in the biomass [22]. The lignin decomposition in SB distributed along a wide range of temperature interval at the end of major degradation zone [23].

Apparatus and procedure

The gasification experiments of SB were carried out in a batch reactor system. The reactor was made of Inconel 625 and the volume of reactor is 10 mL. The designed temperature and pressure are 750 °C and 30 MPa, respectively. The schematic diagram of the experiment system is shown in Fig. 2. The experiment system is composed of six subsystems. The main components of each subsystem are an electric furnace, a batch reactor, a thermocouple, a pressure transducer, and a data acquisition station for monitoring and collecting temperature and pressure data. The electric furnace can be operated to a certain temperature to heat up the batch reactor. The thermocouple was inserted into the reactor to detect the reaction temperature and the pressure transducer was used to detect the pressure in the reactor.

For each experiment run, SB sample and catalyst were mixed and then loaded into the reactor. The deionized water was added into the reactor to the desired concentration. Then, the reactor was sealed by two wrenches manually. The Ar gas was used to expel the air inside the reactor. The purging process was repeated for 3 times to make sure that the air was completely replaced by Ar. Then, the reactor was filled with argon with an initial pressure depending on the desired reaction pressure, and heated up in the electric furnace. After the reactor was heated up to the designed reaction temperature, the reaction temperature was held by adjusting the furnace temperature during the reaction process. After reaction, the reactor was cooled to ambient temperature in water. The gaseous products were collected in an air bag for analysis

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