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Characteristics of pore structure of rice husk char during high-temperature steam gasification

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HIGHLIGHTS

- Pore structure of rice husk char during steam gasification was studied in a fixed bed gasifier.
- The surface of the char generated at higher temperatures has more thermal etching marks.
- The pore structure of rice husk char is the most abundant at 1000 °C with SSA of 316 m^2/g.
- After gasification, the pore size increases, and the SSA is significantly reduced to 1–4 m^2/g.

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ABSTRACT

The characteristics of the pore structure of rice husk char during high-temperature steam gasification was investigated in a fixed bed gasifier. The raw rice husk was heated to various temperatures (600–1400 °C) to generate rice husk char. The yield of rice husk char decreases with char generation temperature. Carbon conversion rate of rice husk char after steam gasification decreases significantly with char generation temperature, which is 91.95% at 600 °C, and 52.51% at 1400 °C. The surface of the rice husk char generated at higher temperatures is rougher with more thermal etching marks. The adsorption and desorption isotherms of char and ash indicate the distribution of the pore size is relatively continuous. The desorption isotherm is greater than the adsorption isotherm at high relative pressure. The amount of adsorption and specific surface area of the rice husk char increase first and then decrease with the rise of char generation temperature. The pore structure of rice husk char is the most abundant at 1000 °C, and the specific surface area is 316 m^2/g. After high-temperature (1000–1200 °C) gasification, the pore size increases, and the surface area of the rice husk ash is significantly reduced to 1–4 m^2/g.

1. Introduction

Biomass gasification with steam is used to increase the economic potential of biomass, generating syngas, bio-oil, and char. During gasification, biomass undergoes drying, pyrolysis, and char gasification. An understanding of the physical and chemical changes of biomass during gasification is key to the design of gasifiers and operating conditions. The great advantage of biomass gasification is to obtain gaseous fuel which keeps 70–80% of the chemical energy of the original fuel and is easier to clean, transport and burn efficiently compared to solid fuel [1]. During gasification, part of biomass remains as a condensable stream (tars) and as carbonaceous solid residue (char). Tars are the most troublesome pollutants of product gas, and are the main technical hurdle for the commercial implementation of biomass gasification. Tars are a complex mixture of organic compounds which condense continuously from several hundreds to room temperature, thus causing operating problems. Clean and high heating value gas is usually produced at a high gasification temperature, and it can be used for power generation [2]. However, high temperature discourages some applications of the biomass char which is the intermediate product - the residue of pyrolysis after removing volatile under the anaerobic or reducing condition. Biomass char has several important applications, such as fuel to produce power by direct combustion [3], starting material for chemically activated carbon production [4], even as a catalyst for tar removal [5]. High temperature may discourage the application as activated carbon because of the decrease of specific surface area and ash fusion causing fouling and corrosion [6]. Therefore, there is compromise between high heating value and clean product gas and high amount of high value char for gasification. And for the purpose of producing high heating value and clean product gas, gasification conditions should be optimized.

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As a by-product, biomass char contains high carbon content, low nitrogen, and sulfur content. It has abundant pore structure, and when gasification with steam, gas of high heating value would be gained due to rich in H_2 and CO [7,8]. It is recognized that the gasification reaction rate of the char is determined by the char structure [9]. In general, pore structure variation during steam gasification under different conditions is different. Steam gasification yields an increase in all pore sizes and increases the macroporosity [10]. The characteristics of wood high-temperature steam gasification in a high temperature fixed bed for hydrogen-rich gas production were studied by Li et al. [11] who found it remarkably effective to produce hydrogen rich gas with high-temperature steam gasification of biomass. The gasification characteristics of peanut shells within the temperature range of 550–900 °C were studied by Natarajan and Sethupathy [12]. Experimental results showed that under the condition of 800 °C, the highest gas efficiency and carbon conversion efficiency were 73.5% and 82.5% respectively, and the gas was mainly composed of H_2, CO, CO_2, and CH_4. A study on biomass char steam gasification producing syngas was carried out by Tu et al. [13], and the results showed that when the reaction temperature was 1000 °C and the flow of steam was 0.285 g/(min g char), carbon conversion rate reached a maximum of 78.7%. The effect of alkali metal on pine pyrolysis and pine tar gasification was studied by Aho et al. [14] who found that alkali metal had a catalytic effect on pyrolysis and gasification. Gasification kinetics of cedar char, cedar bark char, a mixture of hardwood char and lawngrass char produced under the condition of 900–1000 °C were studied by Matsumoto et al. [15]. Due to differences in the alkali metal content and biomass char O/C (molar ratio) of biomass ash, gasification reaction order was a mixture of hardwood char > cedar char > (cedar bark char, lawngrass char).

At present, conventional biomass char gasification concentrates on relative low-temperature (<900 °C) gasification [16–18]. The main problem is the heating value of the product gas is low, and the content of tar is high due to the low conversion rate of carbon during pyrolysis and gasification. Tar can be reduced by thermal cracking that requires heating the tar to a high temperature [19,20], but whether the char generated at high temperatures has abundant pore structures that promote gasification is not clear. This study selected rice husk as the raw material, and the variation of the pore structure of rice husk char during gasification was investigated. The raw rice husk was heated to various temperatures (up to 1400 °C) to generate rice husk char for study the effect of char generation temperature on structural evolution. The char yield with different char generation temperatures and carbon conversion rate of the char gasification with steam at different gasification temperatures (800–1200 °C) were provided. The morphology of the rice husk char and ash was analyzed by scanning electron microscopy (SEM). The pore structure of the rice husk char and ash was characterized. The study will provide an experimental reference for the design of biomass gasifier and operating conditions.

2. Material and methods

2.1. Material

Rice husk, the typical biomass found in Heilongjiang province in was chosen as the raw material. The rice husks are from a rice processing plant. The proximate and ultimate analysis of rice husk are shown in Table 1.

Table 1
Proximate and ultimate analysis of rice husk.

M_{ad}[a]%	V_{ad} %	A_{ad} %	FC_{ad} %	C_{daf}[b] %	H_{daf} %	O_{daf} %	N_{daf} %	S_{daf} %
6.9	59.4	18.9	14.7	49.3	6.1	43.9	0.6	0.1

M: Moisture. V: Volatile. A: Ash. FC: Fixed Carbon.
[a] ad: air-dry basis.
[b] daf: dry, ash free basis.

2.2. Experimental setup and procedures

The high-temperature steam gasification of rice husk char was carried out in a fixed bed gasifier. The experimental setup is shown in Fig. 1. It mainly consists of a steam generator, a fixed bed reactor (length = 800 mm, inside diameter = 50 mm, outside diameter = 60 mm), a condenser and absorption devices.

The rice husk with similar size was put into a sealed crucible, heated in an elevator furnace to 600 °C, 800 °C, 1000 °C, 1200 °C and 1400 °C at a heating rate of 20 °C/min, and maintained at each final temperature for 40 min to prepare the char. Then the rice husk char was dried at the temperature of 105–110 °C for 3 h. The fixed bed reactor was heated with steam fed into the reactor at a flow rate of 1.69 g/min to 1200 °C. The reaction boat, filled with 2 g of rice husk char, was pushed into the reaction zone, and the end of the corundum tube was sealed up. Condensable gas was condensed in the collecting bottle while incondensable gas was dried in the drying bottle. After 6 min, the reaction boat with residues was moved out of the reaction zone for 3 h cooling and drying. The mass of the residues was weighed and measured for calculation and analysis. Each operational condition and result of the experiments were repeated three times for an average value.

2.3. Measuring methods

Char yield η, carbon conversion rate x, and ash content X are calculated by the following equations.

$$\eta = \frac{m_3 - m_2}{m_1} \quad (1)$$

$$x = \frac{m_3 - m_2 - m_4}{(1 - A/\eta)(m_3 - m_2)} \quad (2)$$

$$X = \frac{A}{\eta - (\eta - A)x} \quad (3)$$

where m_1 is the mass of rice husk before pyrolysis; m_2 is the mass of the crucible; m_3 is the mass of rice husk char and crucible at room temperature; m_4 is the mass of the residue after gasification; A is the ash content of rice husk.

The scanning electron microscope EVO18 manufactured by ZEISS was used to measure the surface morphology of rice husk, char, and ash. The specific surface area analyzer ASAP2020 manufactured by Micromeritics was used to analyze specific surface area and pore size distribution of rice husk, char, and ash. The synchronous thermal analyzer STA449C manufactured by NETZSCH was used to do thermogravimetric and differential scanning calorimetry analysis (TG-DSC) of the ash. The X-ray diffractometer D8 ADVANCE manufactured by Bruker Corporation was used to analyze the composition of the ash.

3. Results and discussion

3.1. Yield of rice husk char

Fig. 2 shows the char yield of rice husk with temperature. The yield of rice husk char decreases gradually with the increase of char generation temperature, from 37.1% at 600 °C to 20.2% at 1400 °C. Obviously, the temperature has a significant effect on yield of rice husk char, and volatile will separate out at high temperatures.