



High quality syngas production from microwave pyrolysis of rice husk with char-supported metallic catalysts



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HIGHLIGHTS

- RHC-supported metallic catalysts had good microwave absorption capability.
- Ni/RHC catalyst presented most effective effects on gas production.
- Ni/RHC and Fe/RHC catalysts played pivotal roles in tar conversion.

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ABSTRACT

This study aimed to obtain the maximum possible gas yield and the high quality syngas production from microwave pyrolysis of rice husk with rice husk char and rice husk char-supported metallic (Ni, Fe and Cu) catalysts. The rice husk char-supported metallic catalysts had developed pore structure and catalytic activity for gas productions and tar conversion. The temperature-rising characteristic, product yields, properties of gas products and tar conversion mechanisms were investigated. It was found that three rice husk char-supported metallic catalysts improved the microwave absorption capability and increased heating rate and final temperature. Rice husk char-supported Ni catalyst presented most effective effects on gas production, e.g. the gas yield is 53.9%, and the volume concentration of desired syngas is 69.96%. Rice husk char-supported Ni and Fe catalysts played pivotal roles in tar conversion that less heavy compounds can be detected along with the reduction of organic compound number.

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1. Introduction

As a renewable, inexpensive sustainable and environment-friendly feedstock, biomass has received considerable attention (Chum and Overend, 2001). Biomass is playing significant role as an alternative source for energy and fuel production around the world. Every year, approximately 80 million tons of rice husk are produced worldwide and about 97% of them are produced by developing countries. As an agriculture country, China has the largest rice cultivation region in the world, and rice husk is the main by-product in the milling factory. China produces about 40 million tons of rice husk every year (Fu et al., 2012). Therefore, the use of rice husk for energy not only reduces pollution, but also generates economic benefits.

Thermochemical conversion of biomass such as pyrolysis, gasification, combustion, and liquefaction is becoming an alternative source for energy and fuel production around the

world. It was agreed that pyrolysis is an attractive method to realize the efficient conversion of biomass to high value-added products, such as oil, char or gas by means of optimizing operating conditions and parameters (Dominguez et al., 2003). Conventional biomass pyrolysis systems such as fluidized bed, fixed bed, rotating cone, transported bed, auger or screw have been extensively studied, which mainly focus on the production of bio-oil (Zhang et al., 2013). Only a few studies were performed to obtain the maximum possible amount of high quality gas products from biomass pyrolysis, such as syngas ($H_2 + CO$) (He et al., 2010; Fernández and Menéndez, 2011). For this purpose, microwave pyrolysis seems to be an attractive alternative, because of its uniform and rapid heating rate. Microwave is able to generate microplasmas and hot spots, which promote heterogeneous catalytic reactions and produce greater concentrations of syngas and hydrogen in the gas products than conventional pyrolysis (Dominguez et al., 2008; Huang et al., 2010; Beneroso et al., 2013). In addition, microwave pyrolysis has other advantages including generation of fewer hazardous compounds, better control of the pyrolysis process and higher heating efficiency (Dominguez et al., 2003). Catalytic

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pyrolysis is another way to improve the concentration of syngas, which depends on the characteristics of the catalyst used (He et al., 2010). Catalysis in biomass pyrolysis was mainly used to crack the heavy compounds in order to obtain lighter gases. The catalysts used in catalytic pyrolysis to improve the quality of gas products consist of metallic catalysts (Shen and Yoshikawa, 2014), mainly nickel-based catalysts, alkali metallic catalysts, dolomites (He et al., 2010), olivine, and a combination of metals on mineral substrates (Zhang et al., 2007). For catalytic reactivity and economic reasons, metallic catalysts, such as nickel-based catalysts and iron-based catalysts are considered the most promising for syngas products from catalytic pyrolysis of biomass (Min et al., 2014; Shen et al., 2014). Metallic catalysts are usually supported by metal oxides (e.g., Al_2O_3) or natural materials (e.g., dolomite, olivine) (Wang et al., 2005). These supports are relatively expensive, and the catalyst preparation steps are time and energy consuming. Recently, some researchers found that char-supported metallic catalysts can overcome the above disadvantages, and can efficiently crack the heavy compounds to commercially valuable gas products (Shen et al., 2014). In addition, the low cost char-supported metallic catalyst would be simply gasified to recover the energy without the need of regeneration after deactivation. It is noteworthy that char obtained from pyrolysis has been reported to be an inexpensive microwave absorber and an advantageous additive for preparation of gas products from microwave pyrolysis (Zhao et al., 2014a,b).

To the best of our knowledge, no studies have been aimed at obtaining high quality syngas with char-supported metallic catalyst in microwave pyrolysis. In present study, the temperature-rising characteristic, product yields, properties of gas products and tar conversion mechanisms were investigated with rice husk char and char-supported metallic (Ni, Fe and Cu) catalysts using microwave pyrolysis, in order to obtain the maximum possible gas yield and the highest syngas quality.

2. Methods

2.1. Raw materials

Biomass feedstock used in this study is rice husk, collected from Yangzhou city, Jiangsu Province, China. The rice husk sample was dried at 105 °C for 12 h before each experiment. The ultimate analysis, proximate analysis and higher heating value (HHV) of rice husk (dry basis) were analyzed and the results were shown as follows: C, 39.37 wt.%, H, 5.13 wt.%, N, 0.32 wt.%, ash, 16.53 wt.%, volatile, 70.60 wt.%, fixed carbon, 12.87 wt.% and HHV, 16.58 MJ/kg. The proximate analysis of rice husk sample was carried out based on GB212-91 standard, the ultimate analysis were analyzed with a Vario EL-III elemental (ELEMENTAR Analysensysteme GmbH), and the higher heating value was analyzed by the SDACM3000 calorimeter.

2.2. Catalyst preparation and characterization

Rice husk char (RHC) was prepared by microwave pyrolysis at the power of 700 W in the N_2 atmosphere for 20 min. Rice husk char-supported catalyst was prepared by incipient wetness impregnation. Firstly, 20 g rice husk char was incipient wet-impregnated with 0.04 mol $\text{Ni}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3$ or $\text{Cu}(\text{NO}_3)_2$ using $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ or $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ as precursors, followed by drying at 105 °C for 12 h. Subsequently, the rice husk char containing metal species was heated in a microwave pyrolysis reactor for 20 min at the microwave power of 800 W in an inert gas (e.g., N_2) atmosphere. The solid residues were collected as rice husk char-supported metallic catalysts, noted as “Ni/RHC”,

“Fe/RHC” and “Cu/RHC”, respectively. In addition, to investigate the effect of Ni content in rice husk char-supported Ni catalysts on pyrolysis performances, three different types of rice husk char-supported Ni catalysts (20 g rice husk char was incipient wet-impregnated with 0.02 mol, 0.06 mol and 0.08 mol $\text{Ni}(\text{NO}_3)_2$) were prepared by the same preparation process, which were noted as “0.5Ni/RHC”, “1.5Ni/RHC” and “2Ni/RHC”, respectively. The catalysts were characterized by X-ray diffractometer (XRD, Rigaku Co.). In addition, the pore structure properties of the catalysts were measured via nitrogen adsorption isotherm at 77 K with a Micromeritics instrument ASAP 2020. The specific surface area was analyzed using the Brunauer–Emmett–Teller (BET) model. The amount of nitrogen adsorbed at a relative pressure of $p/p_0 = 0.98$ was used to evaluate the total pore volume.

2.3. Experimental system

A schematic diagram of microwave pyrolysis apparatus is shown in Fig. 1, which consists of eight components: nitrogen cylinder, suspended body flowmeter, specially made quartz fixed bed reactor, two K-type thermocouples, microwave oven, computer, condensing system, and gas sampling bag (20 L).

A 3600 W microwave oven with four magnetrons was used for pyrolysis. The oven was operated at the frequency of 2.45 GHz. A quartz fixed bed reactor (350 mm length, 100 mm outer diameter) was placed inside the oven cavity, and the steam outlet tube of reactor was connected to the condensing system. In this study, two stainless steel-sheathed K-type thermocouples with a diameter of 3 mm were used and the thermocouples sheath was earthed to avoid arcing. In order to maintain an inert atmosphere during the experiments, N_2 with 150 L/h flow rate was passed through the system from the bottom of the reactor for 15 min prior to the commencement of the experiment, and then the oven was turned on. For each experiment, 50 g rice husk blended with 15 g catalysts was put into the quartz reactor, and the microwave output power was set to 700 W for 20 min. The volatiles released from pyrolysis of rice husk were passed through the condensing system which consists of four connected condenser pipes filled with flowing cooling water. Condensable volatiles were recovered from the condensing system by dissolving it in CH_2Cl_2 . It was then subjected to further evaporation to remove the solvent at 40 °C. The non-condensable gas was collected at intervals of 2 min in 20 L Tedlar[®] gas sampling bags. The exit pipeline connected between the exit of the quartz fixed bed reactor and the condensing system was heated by the heating tape to avoid the condensation of condensable volatiles. Solid and liquid yields were calculated from the direct weight of each fraction after the reaction was completed, while gas yields were calculated based on the mass balance. All experiments were carried out in two runs to confirm the values obtained.

2.4. Pyrolysis products analysis

Gas products in the gas sampling bags from microwave pyrolysis were analyzed using an Agilent 6890N gas chromatography (GC) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID) and high-purity argon (99.999%) was used as the carrier gas.

The chemical composition analysis of liquid products was carried out using gas chromatography/mass spectrometry (GC/MS, Agilent 7890A/5975C) with a Varian Cp-sil 8cb capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness). The carrier gas (helium, 99.999%) was set at a constant flow rate of 3 mL/min. The temperature of oven was programmed from 40 to 180 °C at the heating rate of 5 °C/min, and then to 280 °C at the heating rate of 20 °C/min. MS was conducted in the following operational

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