Preparation and Properties of Rice Hull Ash as the catalysis supporter in the fluidized-bed reactor

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Abstract. This research focuses on the preparation and properties of rice hull ash (RHA). We prepared RHA from combustion of rice husk in the fluidized-bed reactor. The temperature field of the furnace was steady and below 850°C to keep SiO2 amorphous. XRD, BET and SEM were applied in the characterization tests to investigate the effect of flow rate (u), the higher primary-secondary wind ratio (i) and relative height of bed material. The optimal combustion condition for preparing RHA was discussed. RHA obtained from rice hull contains abundant amorphous SiO2 (>90%) and the characterization results of RHA show its potential to be a good catalyst supporter.

1. Introduction

Rice husk is constituted by lignin, cellulose and hemicellulose. Inorganic content in rice husk is about 20% which makes the rice husk have relatively high ash content among the agricultural wastes. The inorganic matter in rice husk is mainly amorphous SiO2 and the content of SiO2 in rice hull ash (RHA) can get up to 87%-97%. Because of the high value of specific surface area and activity, SiO2 in amorphous conditions can be applied prospectively in adsorption industry, such as catalysis. SiO2 in rice husk connects with organic material with low porosity and combustion plays an important role in reducing organic material to achieve pore passage and porous structure[1].

Many researchers investigated on how to achieve RHA with high porosity. Combustion of rice husk in a conventional boiler can lead to the rise of crystal SiO2 and the formation of cristobalite and tridymite. Fernandes compared RHA obtained from grate furnace, fluidized bed and suspension combustion and he found that silica in RHA from suspension combustion was amorphous while silica from grate furnace and fluidized bed were crystals[2]. A considerable amount of literature has been published on the effect of combustion conditions on the crystallization of SiO2. Many published papers on this issue show that silica crystal is easily accessed when the temperatures in combustion are over 800°C according to their experimental data[3-5]. Wang employed RHA obtained from combustion under 500°C on the absorption of Cu2+ and it had good performance[6]. Adams studied characterization of RHA and its performance in turbidity removal from water[7]. We employed RHA as catalysis supporter on CO-SCR[8, 9].
In our work, RHA was produced by the combustion of rice husk in a fluidized-bed reactor. Characterizations (structural, morphological, etc.) were employed in order to investigate the effect of combustion conditions on the quality of RHA.

2. Experiment Systems and Characterization Tests

2.1. Fluidized-bed Reactor Experiment System

The Fluidized-bed Reactor (FBR) Experiment System is shown in Fig. 1. A certain amount of Rice husk can be sent into the furnace by screw feeder. Air compressor supplies primary air. Primary air flows through air distributor to fuel with a flow rate of 15-26m/s after wind holes. Primary air at 15-26m/s after wind holes plays a role in turbulent motion of the bed material at the bottom. The inlets of second air and overfire air are respectively 600mm and 1050mm high from the bottom. Cyclone separator and warehouse of ash can collect the rice hull ash for further analysis.

2.2. Characterization Tests

X-ray diffraction (XRD) studies were conducted using the PANalytical X’Pert Pro instrument. Scanning from 10 to 80° was carried out using the 40kv tube voltage and 40mA tube electricity by the step of 0.03°. Brunauer–Emmett–Teller (BET) surface area and pore diameter studies were performed out by degassing the samples under N2 flow. The degassed samples were analyzed in the Microtrac Belsorp-Max Surface Area and Porosity Analyzer. The morphologies of samples were observed by field emission scanning electron microscope (SEM) operated at 15kV (SU-8010).

3. Results and Discussion

3.1. Fluidization and combustion characteristics

Fig. 2 and Fig. 3 show the steady temperature in different height of the furnace with different air distribution. With the two height of bed material, the higher primary-secondary wind ratio (i) makes the temperature distribution more balanced. When i=55:45, the temperature of low zone is relatively low because of not enough oxygen and slow combustion in the zone. The burning hotspot was upon
the inlet of lower secondary air \((h=855\text{mm and } h=1240\text{mm})\) peaked at 850°C. Too high temperature may cause agglomeration and high crystallinity. Thus low \(i\) may be not good for the generation of rice husk ash with low crystallinity. Moreover, too low \(u\) resulted in uniform temperature field in furnace and even fail fluidization. With lower \(i\) like 55:45 more bed material resulted in worse flow and combustion. More bed material promoted uniform temperature distribution in furnace and extending main combustion area. When \(i=70:30\) with 150mm high bed material, the main combustion area is in the top free area of the furnace and the temperature of the furnace is uniform under 850°C.

![Fig. 2 Temperature in furnace (height of bed material:100mm, rate of bed material height and furnace height: 0.050)](image1)

![Fig. 3 Temperature in furnace (height of bed material:150mm, rate of bed material height and furnace height: 0.075)](image2)

### 3.2. Effect of Air Distribution on Properties of Rice Husk Ash

Here we investigated the rice hull ash collected in cyclone separator in condition of different \(i\) and \(u\) with150mm high bed material. Loss on ignition (LOI) was employed to calculate the quantity of active carbon in RHA samples achieved at the critical resident time and it was obtained by comparing the difference between RHA samples’ weight before and after complete combustion in TGA/DSC simultaneous thermal analyser. Fig. 4 shows LOI of ash achieved in different \(u\) and \(i\). Overall burn-off rate of rice husk increased with higher \(i\) due to the better fluidization of bed material. As is shown, the relation of \(u\) and LOI was non-monotone. The longer resident time can help combustion, but lower \(u\) can also weaken fluidization of bed material and turbulence of gas flow in furnace. On the contrary, higher \(u\) can promote fluidization of bed material and turbulence of gas flow in furnace, but the shorter resident time may prevent the burn-off of rice husk.
Air distribution can also affect porosity of rice hull ash. Fig. 5 shows LOI of ash achieved in different \( u \) and \( i \). When \( u=0.5\text{–}0.6\text{m/s} \), agglomeration and porous carbon particles reduced BET of ash. When \( u=0.6\text{–}0.7\text{m/s} \), BET distinctly increased with increasing \( u \). When \( u>0.7\text{m/s} \), BET remained. Therefore, it is likely that \( 0.6\text{–}0.7\text{m/s} \) was the optimal flow rate \( u \) and \( 70:30 \) was the optimal \( i \). In this condition, porosity of rice hull ash and burn-off rate were both expected.

According to the XRD of RHA, \( \text{SiO}_2 \) in RHA obtained in our optimal conditions \( u=0.6\text{m/s} \) was almost amorphous (see Fig. 6). Parts of \( \text{SiO}_2 \) in RHA obtained at \( u=0.8\text{m/s} \) was quartz, because of
3.3. Effect of Bed Height on Properties of Rice Husk Ash

Height of bed material can affect combustion of rice husk by fluidization of bed material. Fig. 7 shows LOI in different $u$ and $i$. 150mm has 0.075 rate of bed material height and furnace height and 100mm high bed material has 0.050 rate of bed material height and furnace height. Burn-off rate of rice husk with 150mm high bed material was higher because of better turbulence of rice husk in furnace. When $i=70:30$, fluidization of bed material was better and rice husk had higher burn-off rate and lower LOI. Although high wind speed can also intensify turbulence, the extending main combustion area in the top free area (see Fig. 2 and Fig. 3) may cause that more unburned carbon particle was toke along by flow into cyclone separator.

Fig. 7  Effect of rate of bed material height and furnace height on LOI of ash

Fig. 8 show the effect of rate of bed material height and furnace height on porosity of rice hull ash. Ash had higher BET when rate of bed material height and furnace height was 0.050. It is almost certain higher BET is a result of shorter resident time in smaller main combustion area and weaker fluidization of bed material. When $u=0.8\text{m/s}$, rice hull has shortest resident time and BET reached 45.22m$^2$/g. Moreover LOI was low in $u=0.8\text{m/s}$ and 0.050 rate of bed material height and furnace height (see Fig. 7). The temperature of furnace retains lower than 800$^\circ\text{C}$ and SiO$_2$ in rice hull ash was almost amorphous here. Therefore $i=70:30$, $u=0.7\text{m/s}$ and 0.050 rate of bed material height and furnace height was also a good condition for producing rice hull ash with amorphous SiO$_2$. When rate of bed material height and furnace height was 0.075, BET peaked 24.83m$^2$/g. Therefore here in this FER, 0.075 rate of bed material height and furnace height was optimized with the $i=70:30$ and $u=0.7\text{m/s}$.

Fig. 8  Effect of rate of bed material height and furnace height on BET ($i=70:30$)

Based on the data, the combustion of rice husk in FBR can be influenced by air distribution and bed height together. Low $u$ can give rice husk more resident time, but it can weaken turbulence of bed material and slow down the rate of combustion; High rate of bed material height and furnace height
can promote turbulence of bed material and give rice husk more resident time, but it may result in that main combustion area in is in the top free area of the furnace. Therefore, we picked optimal conditions to help the complete combustion of rice husk and gain polyporous rice hull ash with low crystallinity of SiO$_2$.

4. Conclusion
This paper presents research on the preparation and properties of RHA. We prepared RHA from combustion of rice hull in the fluidized-bed reactor. The characterizations of RHA were investigated to analyse the effect of combustion conditions on the quality of RHA. Based on the experimental results and discussion, conclusions can be obtained as follows:

1. Through controlling of $i$ and height of bed material, the temperature of the furnace is uniform under 850°C. The fluidized-bed reactor is applicable to preparing RHA in the industry.

2. We optimized 0.075 as the rate of bed material height and furnace height, $i=70:30$ and $u=0.7$m/s. The RHA simples obtain in the optimized conditions were polyporous with relatively high burn-off rate and low crystallinity of SiO$_2$. The RHA shows its potential to be a good catalysis supporter.

References
[1] T. H. Liou. Preparation and characterization of nano-structured silica from rice husk. Materials Science & Engineering A. 2004, 364: 313-323.
[2] C. D. Fernandes I J, Kieling A G. Characterization of rice husk ash produced using different biomass combustion techniques for energy. Fuel. 2016, 165: 351-359.
[3] R. S. Bie, X. F. Song, Q. Q. Liu, X. Y. Ji, P. Chen, R. S. Bie, X. F. Song, Q. Q. Liu, X. Y. Ji and P. Chen. Studies on effects of burning conditions and rice husk ash (RHA) blending amount on the mechanical behavior of cement. Cement & Concrete Composites. 2015, 55: 162-168.
[4] Q. Feng, H. Yamamichi, M. Shoya and S. Sugita. Study on the pozzolanic properties of rice husk ash by hydrochloric acid pretreatment. Cement & Concrete Research. 2004, 34: 521-526.
[5] M. A. Hamad and I. A. Khattab. Effect of the combustion process on the structure of rice hull silica. Thermochimica Acta. 1981, 48: 343-349.
[6] Wang, L. C. I and W. F. C. Kinetic study of adsorption of copper (II) ion from aqueous solution using rice hull ash. Journal of the Taiwan Institute of Chemical Engineers. 2010, 41: 599-605.
[7] F. V. Adams, B. D. Ikotun, D. O. Patrick and A. F. Mulaba-Bafubiandi. Characterization of Rice Hull Ash and Its Performance in Turbidity Removal From Water. Particulate Science & Technology. 2014, 32: 329-333.
[8] Z. Teng, S. Huang, L. Fu, H. Xu, N. Li and Q. Zhou. Study of a catalyst supported on rice husk ash for NO reduction with carbon monoxide. Catalysis Science & Technology. 2020, 10: 1431-1443.
[9] Z. Teng, L. Fu, N. Li and Q. Zhou, Selectivity catalytic reduction of NO by CO over Fe-Cu oxides supported on rice hull Ash(Rha), in: 7th International Conference on Power Engineering, ICOPE 2019, October 21, 2019 - October 25, 2019, International Conference on Power Engineering-2019, Kunming, China, 2020, pp. 570-574.