



## Full Length Article

# Surface characterization studies of walnut-shell biochar catalysts for simultaneously removing of organic sulfur from yellow phosphorus tail gas



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## ABSTRACT

The influences of different preparation conditions for surface characteristics on removing organic sulfur were studied. From BET, XRD, FTIR, DRIFTS, TG/DTA, CO<sub>2</sub>-TPD results, it can be seen that these preparation conditions had great influences on the pore structure, specific surface area, crystal structure and surface functional groups. The micropore volume, amorphous structure and alkalinity site strength played major roles in desulfurization process. H<sub>2</sub>S was oxidized by oxygen containing functional groups, such as —COO, —C=O. H<sub>2</sub>O molecule could be converted into some groups, such as —CH and C—OH groups, and promoted the hydrolysis reaction. The strong alkalinity site was the key factor for chemical adsorption and hydrolysis. H<sub>2</sub>O molecule, —CH, C—OH groups promoted the hydrolysis reaction and —COO, —C=O groups promoted the oxidation of H<sub>2</sub>S on the surface of WSB. Meanwhile, the main desulfurization process over WSB after carbonization was adsorption and it changed to hydrolysis reaction after activation on the surface of WSB. Furthermore, the reaction mechanism was investigated by DRIFTS measurement according to the change of surface functional groups.

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## 1. Introduction

CS<sub>2</sub> (carbon disulfide) and COS (carbonyl sulfide) exist widely in chemical raw material gas and industrial waste gas, particularly in the yellow phosphorus tail gas. CO (carbon monoxide) of yellow phosphorus tail gas can be used for the one carbon chemical industry. However, CS<sub>2</sub> and COS can not only corrode pipeline equipment, but also poison the catalysts in the subsequent process and reduce the purity of CO. Therefore, the removal of CS<sub>2</sub> and COS is necessary. Removal method of CS<sub>2</sub> and COS includes wet process and dry process. The wet methods include organic amine absorption and liquid phase catalytic hydrolysis [1,2]. Compared with the wet process, the dry process, such as adsorption, hydrolysis, hydrogenation and oxidation, characterizes high sulfur resistance [3–5], low operation cost [6–8] and low secondary pollution [9–11]. Particularly, catalytic hydrolysis characterizes less side effects, mild reaction conditions, cheapness, fewer by-products and higher con-

version efficiency. Therefore, it has grown up to become a focus of current research.

The selection of the catalyst support is the key factor in the preparation of the supported catalyst. In recent years, the biochar has been widely concerned because of its widely application in agriculture, environment, energy and other fields [12–15]. Biochar characterizes better micropore structure and larger specific surface area. Meanwhile, more functional groups generated on the surface of biochar (such as O—H and C=O groups on the surface of corn cob biochar for adsorption of ammonium [16], O—H and surface oxygen functional groups on the surface of potato stem biochar for adsorption of Norfloxacin (NOR) [17]), which shows better activity than activated carbon in the aspects of adsorption (such as accumulated phosphorus is 2.6 gP/kg lodgepole pine wood based biochar and 1.9 gP/kg coal-based activated carbon [18]) and catalysis (such as higher reduction of Hg(II) by bagasse and hickory chips based biochar than activated carbon [19]). Yunnan Province has abundant biochar resources, such as straw, walnut shell, cigarette rod bamboo. For example, Yunnan Province is China's major walnut producing areas, which accounts for about 1/3 of domestic production (about 600,000 t/a). If a large number of walnut shells (about 250,000 t/a) discard or burn, it would cause serious waste of resources. Preparing biochar using cheap biomass waste can

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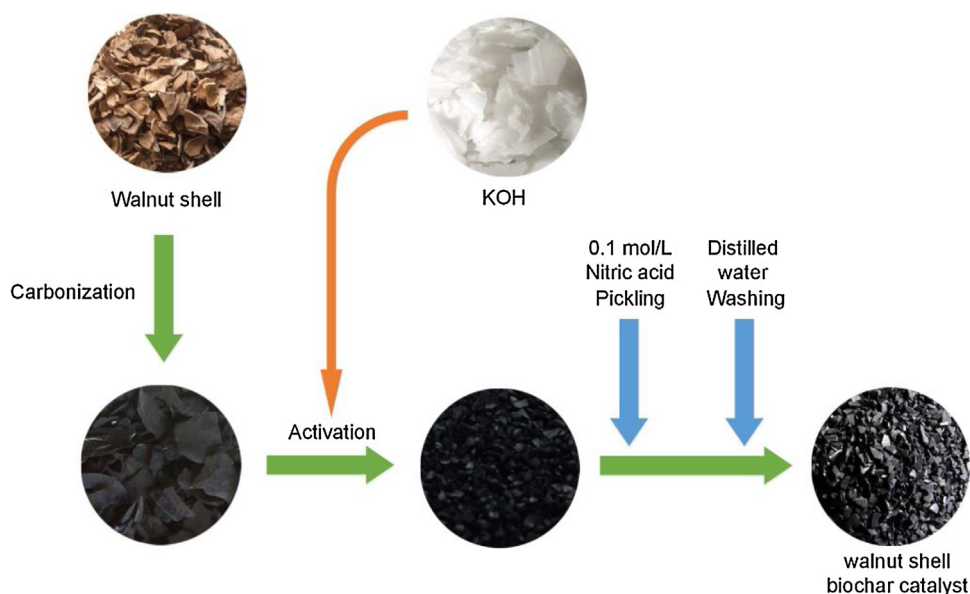


Fig. 1. Preparation process of walnut shell biochar catalyst.

solve the problem of biomass waste disposal and utilize. It also can achieve the goal of sustainable development [20–25]. As an inexpensive precursor [26], walnut shell has high fixed carbon content [21], low ash content [27]. Activated carbon derived from walnut shell has high surface area [25] and high pore volume [22]. Alighardashi et al. prepared walnut shell biochar with  $\text{H}_3\text{PO}_4$  activation, which has high surface area ( $1434.6 \text{ m}^2/\text{g}$ ) and high pore volume ( $0.747 \text{ cm}^3/\text{g}$ ) [21]. Catarina et al. prepared walnut shell biochar by pyrolysis, which has low ash content (0.5%) [27]. Yu et al. prepared walnut shell biochar with KOH activation, which has high surface area ( $1881 \text{ m}^2/\text{g}$ ) and high pore volume ( $0.899 \text{ cm}^3/\text{g}$ ) [25]. Therefore, walnut shell biochar has a wide application prospect. Although many researches had focused on the preparation and characterization of biochar catalyst, few researches were focused on the relation between surface characteristics and reaction, especially for the hydrolysis reaction of organic sulfur gases.

In this study, the walnut shell was used to prepare biochar catalyst. Meanwhile, through the adsorption and catalytic hydrolysis process, the  $\text{CS}_2$  and COS could be simultaneously removed. The influences of different preparation conditions for surface characteristics on removal of  $\text{CS}_2$  and COS were investigated, such as carbonization temperature, alkali species, alkali content and activation temperature. In addition, for the purpose of further illustrating the effect of preparation conditions, DRIFTS (Diffuse reflectance infrared Fourier transform spectroscopy), TG/DTA (Thermogravimetric/Differential Thermal Analysis),  $\text{CO}_2$ -TPD ( $\text{CO}_2$  Temperature Programmed Desorption), FTIR (Fourier Transform Infrared Spectroscopy), XRD (X-Ray Diffraction) and BET (Surface area and pore structure Analysis) test methods were used to investigate the surface characteristics in this study. Meanwhile, the reaction mechanism was investigated by DRIFTS measurement according to the change of surface functional groups.

## 2. Experimental

### 2.1. Materials preparation

The removal efficiency of  $\text{CS}_2$  and COS over biochar catalysts derived from different natural resources was showed in Fig. S1 (Supplementary Materials). From Fig. S1, it could be found that walnut shell biochar had the best removal efficiency of  $\text{CS}_2$  and COS. From Fig. S2, it could be found that  $\text{H}_2\text{S}$  desorbed from the surface

of biochar. It indicated that biochar had a little catalytic hydrolysis effect. However, wood biochar desorbed less  $\text{H}_2\text{S}$  than apricot shell biochar, which indicated that wood biochar had less hydrolysis activity. Furthermore, the adsorption of  $\text{CS}_2$  and COS were the main removal process on the wood biochar. From Fig. S3, by comparing with different periods of walnut shell (derived from mature and immature walnut), it could be found that biochar derived from mature walnut shell has higher desulfurization efficiency, which is attributed to the high carbon content (45.27% in mature walnut shell and 22.14% in immature walnut shell). By comparing with different growing locations of walnut shell (derived from Yunnan Province and Xinjiang Province in China), it could be found that there is no obvious difference for removing  $\text{CS}_2$  and COS between different growing location. Because Yunnan Province is China's major walnut producing areas, according to above experiment results, the mature walnut shell derived from Yunnan Province was chosen in this study.

The walnut shell comes from Kunming (Yunnan Province) was used to prepare biochar in this study. The preparation process was showed in Fig. 1. The walnut shell was carbonized in the pipe furnace under the nitrogen environment at  $600\text{--}900^\circ\text{C}$  (the heating rate was  $5^\circ\text{C}/\text{min}$ ) for 60 min, and then activated with different activating agents (such as KOH, NaOH,  $\text{KHCO}_3$  and  $\text{NaHCO}_3$ , the ratio of activating agent to carbon of 1:1–4:1) in the pipe furnace under the nitrogen environment at  $600\text{--}1000^\circ\text{C}$  (the heating rate was  $5^\circ\text{C}/\text{min}$ ) for 60 min. Next, the walnut shell biochar was washed with 0.1 mol/L dilute nitric acid for removal of ash and activating agent, and washed with distilled water to a constant pH (pH=7), and then dried at  $120^\circ\text{C}$  for 4 h in the drying oven. This material is identified as WSB-XXY. The WSB represented the walnut shell biochar, and the XX represented the influence factors, such as CT (carbonization temperature), RAC (the ratio of alkali to carbon), AT (activation temperature). The Y represented the numerical values of the corresponding factors. For example, the WSB-CT600, WSB-CT700, WSB-CT800 represented that the walnut shell biochar was carbonized at  $600^\circ\text{C}$ ,  $700^\circ\text{C}$ ,  $800^\circ\text{C}$ , respectively, and the other preparation conditions were same.

### 2.2. Characterization

XRD patterns were collected using a D/MAX-2200 diffractometer fitted with a Ni-filtered  $\text{Cu K}\alpha$  radiation ( $\lambda=0.15406 \text{ nm}$ )

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