



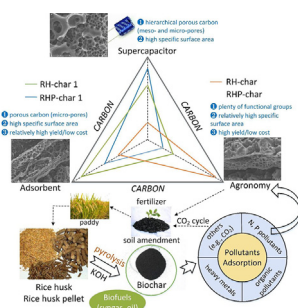
Micro-mesoporous carbons from original and pelletized rice husk via one-step catalytic pyrolysis

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GRAPHICAL ABSTRACT



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ABSTRACT

This paper studied the KOH-catalyzed pyrolysis of rice husk (RH) and its pellet (RHP) at a high temperature (750 °C) for activated bio-carbons production. The mass ratio of KOH and biomass greatly impacted the pyrolysis kinetic and biochar property. The KOH catalysis (mass ratio: 1) reduced significantly the activation energy to 41 kJ/mol. During carbonization with KOH, the in-situ generated K_2CO_3 tailored the morphology and size of the self-template (SiO_2 nanoparticles), giving rise to the chars with the open foam-like porous architectures enrich in micro- and meso-pores. Thus, the KOH activation via one-step pyrolysis could produce the micro-mesoporous carbons (e.g., RH-char 1 and RHP-char 1) with high specific surface areas and high content of oxygen-functionalities. Furthermore, the hierarchical porous carbons have high potential applications in adsorption process and electrochemical energy storage (e.g., supercapacitor) because of their unique physicochemical properties.

1. Introduction

Pyrolysis has been regarded as one of the promising thermochemical technologies for converting biomass or polymer to energy and chemical products (Kan et al., 2016). Depending on heating rate and residence time, pyrolysis of biomass is classified into slow, fast and flash pyrolysis aiming to maximize the yield of either bio-oil or bio-char (Kan et al., 2016). Additionally, maximized gas yields could be achieved via

catalytic pyrolysis at relatively high temperatures (Shen, 2015b). Biomass pyrolysis generally follows a three-step mechanism comprising of dehydration, primary and secondary reactions. Among them, dehydrogenation, depolymerization and fragmentation are the competitive reactions during the primary decomposition of biomass. A number of parameters influence the yields and properties of the products, such as biomass type, pretreatment (e.g., physical, chemical, and biological), pyrolysis temperature, heating rate, and vapor residence time (Shen

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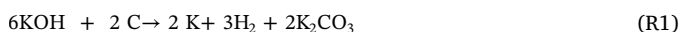
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et al., 2016).

The catalytic pyrolysis of biomass is an approach that is reliable for producing quality renewable fuel and chemical precursors. The bio-oil usually contains high oxygenates fractions that deteriorate the fuel properties. Catalysts can upgrade the bio-oil via selected bond cleavage reactions including deoxygenation, cracking, decarbonylation and others. In usual, bulk and supported acid or base catalysts (e.g., ZSM-5) can tailor the production of high-grade bio-oil in the biomass mediate-temperature pyrolysis (Kabir and Hameed, 2017). Various metal-based catalysts have been developed such as noble metals (e.g., Pt) (Shen and Yoshikawa, 2013), and non-noble metals (e.g., Ni, Fe) (Shen et al., 2014a) for producing high-grade syngas (e.g., low yield of tar, high yield of H₂) during biomass pyrolysis at relatively high temperatures (> 700 °C). Besides, the minerals in biomass such as alkali and alkaline earth metals (AAEMs) had good catalytic performances on pyrolysis of biomass (Hu et al., 2015). Significantly, the pyrolysis vapors can be upgraded including tar and soot reduction (Umeki et al., 2017). Potassium as a kind of AAEMs exists in nature (e.g., clays in soil), which is also a nutrient adsorbed by the plants (Binner et al., 2017). The presence and addition of potassium catalysts can improve the pyrolysis efficiency and upgrade the pyrolysis vapor. Furthermore, potassium in the char enhances the gasification and activation of carbon to produce the syngas or activated carbon (Shen et al., 2017). The potassium in the char can be used as a fertilizer in agronomy (Tan et al., 2017).

In terms of porous carbons production, KOH has been widely developed for chemical activation of char. The mechanism of KOH activation was proposed as the reactions (R1–R4). The KOH activation occurred at the temperature point of 700 °C. Thus, the activated carbon was produced at 750 °C from rice husk char (Nam et al., 2018).



Two-step synthesis has been widely used for production of activated carbons (Zubrik et al., 2017). In the first step, biomass is carbonized at relatively low temperatures (< 500 °C) to produce bio-oil and bio-char. In the second step, bio-char is activated via chemical (e.g., KOH) or physical (e.g., H₂O) approach at relatively high temperatures (> 700 °C) to produce the activated carbon. However, one-step synthesis of activated carbons has gained much attention (Tian et al., 2018). It was seen that catalytic pyrolysis of biomass with KOH could improve the decomposition efficiency and the products quality (Di Blasi et al., 2017). In addition, activated carbons from biomass via the one-step synthesis could be applied for flue gas adsorption (e.g., CO₂) (Saha et al., 2018) and supercapacitors (Zou et al., 2018).

Rice husk (RH) is an agricultural bio-waste abundantly available in the rice-producing countries (Alvarez et al., 2014). Presently, the combustion is a major disposal method, giving rise to considerable pollution of the environment (Yang et al., 2015). However, it is a lignin-rich biomass that can be converted into the fuels (e.g., oil, syngas) via pyrolysis with non-noble metal catalysts (Shen et al., 2015a,b). Additionally, high-quality activated carbons were produced from the lignin-rich biomass via two-step chemical activation with KOH (Correa et al., 2017). Up to date, there is no research work on the co-pyrolysis of RH (especially for its pellet) with the solid KOH. This paper aims to comparatively study the catalytic effect of KOH on slow pyrolysis of RH and its pellet. Furthermore, the activated bio-chars via the one-step synthesis were characterized.

Table 1
Properties of RH and RHP.

	RH	RHP
Bulk density (kg/m ³)	99.6	600
Particle size (mm)	8	9
<i>Proximate analysis (wt%, as received)</i>		
Moisture	6.13	7.33
Volatile matter (VM)	58.17	62.85
Fixed carbon (FC)	19.81	20.42
Ash	15.89	9.40
<i>Ultimate analysis (wt%, dry & ash-free)</i>		
Carbon (C)	36.99	38.13
Hydrogen (H)	5.20	6.03
Nitrogen (N)	0.32	0.66
Sulfur (S)	0.2	0.1
Oxygen (O)	35.27	45.68
H/C	1.69	1.90
O/C	0.72	0.90
HHV ^a (MJ/kg)	15.2	16.2
<i>Ash composition (wt%, as received)</i>		
SiO ₂	93.50	98.18
Al ₂ O ₃	0.18	0.20
CaO	0.36	0.13
K ₂ O	1.20	0.10
Na ₂ O	0.83	0.12
MgO	0.31	0.15
Fe ₂ O ₃	0.24	0.12
P ₂ O ₅	0.45	0.31
SO ₃	0.52	0.24
Others ^b	2.41	0.45

^a HHV (higher heating value) = 0.2949C + 0.825H; (Channiwala and Parikh, 2002).

^b By difference.

2. Materials and methods

2.1. Feedstocks and chemicals

RH were collected from a grain-processing enterprise in Jiangsu province, China. And RH pellet (RHP) was obtained from a biomass pellets production enterprise in Jiangsu province, China. The detailed properties of the feedstocks such as proximate analysis, ultimate analysis and ash composition were shown in Table 1. The bulk density of RHP was much higher than that of RH (approximately 6 times). The volatile matter and fixed carbon presented similar values. However, the ash content of RHP was lower than that of RH caused by the ash removal by the pelletizing process, thereby improving the fuel property of RH (e.g., heating value). Besides, the relatively low contents of S and N in RH and RHP indicated low emission of NO_x and SO₂ during thermochemical processes. All chemicals (e.g., KOH) used in the experiments were the analytical purity, which were purchased from Sino-pharm (China).

2.2. Pyrolysis for bio-chars

The experimental setup for the pyrolysis process is mainly composed of four parts: carrier gas system, pyrolysis reactor, cooling system and gas collection/analysis (as illustrated in Fig. 1). Firstly, the biomass (i.e., RH, RHP) was mixed with the solid KOH by ball-milling (1000 r/min, 30 min). The mass ratios of KOH and biomass were 1:1, 2:1 and 3:1. After that, the solid mixture was fed into the thermal reactor. Prior to the pyrolysis process, the nitrogen (N₂) gas with a flow rate of 0.5 L/min was continuously led into the reactor for 30 min to remove the air. As the pyrolysis was started, the target temperature of the reactor was set as 750 °C with a heating rate of 20 °C/min. The residence time was 2 h to ensure a complete pyrolysis at 750 °C. Finally, the main products including oil (tar), gas and char were collected separately. The char was treated by the washing process with distilled water to remove the

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