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Experimental study on pyrolysis tar removal over rice straw char and inner pore structure evolution of char

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ABSTRACT

A lab scale two staged hot rod reactor was constructed to stimulate the two staged downdraft biomass gasifier. The present study focused on the heterogeneous conversion of the pyrolysis tars over biomass char. A typical Chinese agricultural waste, the rice straw, was chosen for the raw material and the source of the biomass char. Effects of the temperature, the presence of the char and pretreatments of the char, including the water washed char and the char added with K_2CO_3 powder, on the pyrolysis tar removal were investigated. The products of tars were qualitatively and quantitatively analyzed. The evolution of the inner pore structure of chars with different temperatures and residence times was also investigated. The char bed condition exhibited higher tar conversion efficiency than the thermal cracking condition. The results indicated that the presence of the char could catalytically promote the formation of alkyl monoaromatics and meanwhile inhibit the formation of PAHs (polycyclic aromatic hydrocarbons) from the primary tars. The alkali metal elements might play a key role for the catalytic effect of the char. The appropriate increases in the temperature and the residence time for the char production could promote the development of the micro pores in chars.

1. Introduction

The growing environmental requirement for reducing the greenhouse gas emissions and the depletion of fossil fuels have made the search and R&D (research and development) activities for alternative energy sources more urgent than ever. Biomass resources are sustainable, carbon-neutral and estimated to be the fourth largest source of energy in the world, accounting for 10–14% of primary energy i.e. 46 EJ/yr [1]. In China, about 1300 million tons of biomass waste is produced every year, including 789 million tons of agricultural byproducts mostly from rice, corn, and wheat [2]. As one of the promising biomass thermochemical conversion technologies, gasification has attracted more attentions in the recent few decades. It offers a high flexibility in using different kinds of feedstock materials, multiple uses of the syngas including heat, power, biofuels, chemicals etc. and a high process efficiency for utilizing biomass [3]. However, the tar problems are the major obstacle to developing the biomass gasification technology. The tars which have experienced the formation and secondary reactions during gasification processes are finally present in the syngas, resulting in the blocking and corrosion problems in the downstream processes [4]. The methods for tar removal consist of treatments inside the gasifier (the primary method) and the hot gas cleaning processes after the gasifier (the secondary method). The primary method focuses on inhibiting the tar formation by optimizing the operation conditions and design of the gasifier, eliminating the expensive post-gasification removal processes [5]. Two staged downdraft gasifier has been proven to be an effective gasification technology to produce low tar-containing syngas. Different from the traditional gasifier, it is spatially separated into two sections, i.e. the pyrolysis section and the gasification section. The combination of the homogeneous partial oxidation of tars in the throat section and the heterogeneous destruction of tars in the char bed section could make the tar concentration in the syngas of the gasifier less than 5 mg/Nm^3 [6,7].

It was reported that pyrolysis tars yielded from coals, if made to be in contact with a hot carbonaceous surface, could be reduced by a great amount [8,9]. The activated carbon was observed to selectively remove tar species [10]. Boroson et al. [11] found that a thermally stable fraction of newly formed pyrolysis tars from sweet gum hardwood was very reactive in the presence of the wood char. This fraction was oxygen containing aromatic tars which was mostly originated from the lignin. Brandt et al. [12] conducted a pilot scale two staged downdraft gasifier and found that the char bed section was effective in eliminating the PAHs (polycyclic aromatic hydrocarbons) type of tars. Abu et al. [13] discovered that at 900 °C the conversion of phenol over biomass char was dominated by thermal cracking whereas the conversion of naphthalene was dominated by catalytic conversion. Hosokai et al. [14] concluded from the results of heterogeneous conversion of tars, that more fused rings of the aromatic tars, more reactive the tars were to

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be decomposed. Some research groups have investigated the removal of mixture tars from pyrolysis/gasification by biomass char [15–20]; most of them proved that the chars were very effective in reducing the tar species [15–17,19,20]. However, it was argued that the thermal cracking was the main mode of tar decomposition and the presence of char could promote the tar cracking but not to a sufficiently high extent. It might be due to the larger size of the wood char used and lack of the oxidizing atmosphere for char activation [18].

The atmosphere is also an important factor for the tar destruction over biomass char, as it will decide the specific reaction pathways, for example the inert atmosphere leads to the cracking pathway and the oxidizing atmosphere leads to the reforming pathway. Morf et al. [17] concluded from the comparison of heterogeneous and homogeneous conditions that the presence of char could accelerate the conversion of tars rather than changing the conversion pathways. Hosokai et al. [14] investigated the effects of different atmospheres, the presence/absence of H_2 and steam, on the tar removal by char. They found that coking was the main mechanism for tar removal even with the steam in the atmosphere. Fuentes-Cano et al. [21] found that the presence of steam in the atmosphere could reactivate the coked char for catalytic removal of tars. Nitsch et al. [22] concluded that the wood char was highly catalytic with phenol (the model tar) in the presence of steam and the hydrogen showed little influence on the catalytic activity of char. The above reviews show that the mechanism of tar removal by biomass char is still in dispute and not very clear, which greatly depends on the composition of input tars and the atmosphere. Thus it is necessary to use more precise experimental devices and tar sampling and detection methods to investigate this topic.

The role of biomass char in the process of tar removal is considered as the catalyst [19,23] as well as the adsorbent [24]. The physical and chemical microstructures are greatly related to the performance of the char. Griffiths et al. [10] attributed the cracking of tars to the temporary immobilization of tars on the surface of the activated carbon. Ekström et al. [16] explained the better performance of char in tar removal compared with the pure ash as the higher inner surface of the char. Bhandari et al. [25] concluded that the char with larger specific surface area and pore volumes showed higher removal efficiency of toluene. Burhenne et al. [26] found that the surface area of micropores above 700 m^2/g was a good indicator for char to crack benzene at high temperatures. Moliner et al. [27] reported that the initial reaction rate of methane cracking was related to the surface chemistry of the activated carbons, whereas the long-term behavior was related to the physical pore structure of the catalyst. Additionally, Dabai et al. [20] showed that the types and particle size of char had little influence on the tar removal by biomass char. Above reviewed works mainly focus on the effect of the physical microstructure of char on tar removal; however the active sites of the char as a catalyst in reducing tars have rarely been reported.

It was also reported to use biomass char as the catalyst support for tar removal, due to its porosity and thermostability. Kastner et al. [28] found that the iron supported biochar could lower the activation energy of toluene conversion by 47% and decrease the formation of benzene relative to biochar alone. Zhang et al. [29] compared the tar removal performances for biomass/coal char supported iron catalyst and biomass char in a novel pilot gasifier and found that the biomass char supported iron catalyst showed much higher activity for tar reforming. Min et al. [30] concluded from results that the char-supported iron/nickel catalysts showed higher activity for tar reforming than the char itself. They also found the char could interact with the catalysts to improve the catalyst activity for steam reforming of tar. Shen et al. [31] embedded the silica-based nickel nanoparticles into the carbon matrix of rice husk char through impregnation/pyrolysis method. The synthesized catalyst showed high tar conversion efficiency, up to 96.5%.

A lab scale two staged hotrod reactor was constructed in our research group to stimulate the downdraft two staged gasifier. The first stage of the reactor represents the pyrolysis section of the gasifier and the second stage of the reactor represents the gasification section in the gasifier. Our previous study focused on the formation and homogeneous conversion of tars with different oxidizing agents using this reactor [32]. The objective of the present study is to explore the role of biomass char in heterogeneous conversion of pyrolysis tars and provide optimization strategies for the real gasifier. A typical Chinese agricultural waste, rice straw, was used for the raw material as well as the source of the char. The effects of the temperature, the presence of the char and the addition of potassium carbonate in char on the pyrolysis tar removal were investigated. An accurate tar sampling method was performed and the tars were qualitatively and quantitatively analyzed. The evolution of the inner pore structure of chars with different temperatures and residence times was also investigated.

2. Materials and methods

2.1. Materials

The biomass material chosen in this paper was rice straw received from Chongming Island, Shanghai. The proximate and ultimate analysis for rice straw was shown in Table 1. Sample was sieved into small size with a diameter range of 100–150 μm by KER-1/100A sealed sample preparation mill from Zhenjiang Kerui Zhiyang Shebei Co. Ltd., then was dried at an oven temperature of 30 °C for 12 h before being used.

The char bed used in the second stage was produced in Macro-TG platform by pyrolysis of rice straw with a diameter range of 100–150 μm. Specifically the raw material was heated at 30 K/min from ambient to 500 °C, then was held for 1 h. Subsequently it was cooled down and stored in glass bottles. The two kinds of pretreated char, including the water washed char and the char added with K_2CO_3, were prepared as follows: the char was first washed by immersed in the deionized water for 2 h then was dried in oven at 95 °C for 24 h to finally make the water washed char. The K_2CO_3 powder previously ground was added into the water washed char and was physically mixed with it to produce the char with K_2CO_3. The K_2CO_3 used in the present paper was analytical reagent from Sinopharm Chemical Reagent Co., Ltd, with purity of ≥99.0%. The ground K_2CO_3 powder was with the particle size range of 74–425 μm. The mass of K_2CO_3 powder added to the water washed char was about 0.04 g, which was 8% of the mixture on mass basis.

2.2. Macro-TG and procedures

As shown in Fig. 1, Macro-TG was used to produce biomass chars with different pyrolysis temperatures and heating rates. The reactor was made of a quartz tube with a length of 1 m and an inner diameter of 80 mm. It was heated by three sections (top, center and bottom) of

Table 1
Proximate and ultimate analysis of rice straw.

Proximate analysis [a] (wt.% as received)	
Moisture	13.45
Volatiles	62.79
Fixed carbon (by diff.)	15.92
Ash	7.84
Ultimate analysis (wt.% as received)	
C [b]	35.58
H [b]	4.63
O (by diff.)	37.36
N [c]	0.94
S [d]	0.2
Q [e] (MJ/kg) [46]	14.16

[a] GB/T 212-2008.
[b] GB/T 476-2008.
[c] GB/T 19227-2008.
[d] GB/T 214-2007.
[e] High heating calorific value.