



Effects of K and Ca on reforming of model tar compounds with pyrolysis biochars under H₂O or CO₂



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HIGHLIGHTS

- More functional groups are formed on K-loaded biochar than Ca-loaded biochars.
- Release of K from biochar is nearly twice as that of Ca during tar reforming.
- H₂O or CO₂ activation increases lattice defects and functional groups in biochars.
- Tar reforming pathways include homogeneous reforming and H₂O/CO₂ consumption.

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ABSTRACT

Pyrolysis biochar is widely used as the catalyst for tar cracking during biomass gasification. K and Ca in pyrolysis biochar affect the reforming of biomass tar under H₂O or CO₂ atmosphere significantly. In this paper, the transformation mechanism of H-form/K-loaded/Ca-loaded biochar structures and the reaction route of model tar compounds catalytic reforming were identified. The results show that during the reforming of model tar compounds in 15% H₂O or pure CO₂ at 800 °C, the release of K from biochar samples is nearly twice as that of Ca. More O-containing functional groups are formed on K-loaded biochar than Ca-loaded and H-form biochars. H₂O or CO₂ activation increases the lattice defects and surface functional groups in biochars to promote the combination between biochar and model tar compounds. The pathways for tar reformed in H₂O or CO₂ by K and Ca in biochar include direct homogeneous reforming and consumed by H₂O or CO₂ gasification on biochar surface. Tars containing heteroatoms are converted faster than those containing aliphatic chains and pure aromatic rings. On catalytic reforming of naphthalene and toluene with biochars, in 15% H₂O atmosphere the effect of K is about 10% greater than that of Ca, while in pure CO₂ atmosphere the effect of K is approximately 5% greater than that of Ca.

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1. Introduction

Biomass gasification is gaining attention as a route for the use of biomass energy, but syngas produced by this process usually contains unacceptable levels of tar. Tar control and conversion are key issues for the successful use of biomass-derived products [1]. Among several methods for tar elimination, catalytic reforming [2–6] is considered to be the most promising for large-scale applications, because of the high reaction rate, high reliability and increasing quantity of usable gases. Tar elimination by efficient catalytic conversion by inert carbon-based catalysts are attractive

methods for commercializing this technique. Pyrolysis biochar is widely used as the low-cost catalysts in the cracking of tar in the process of biomass gasification. As for the biomass gasification technology, steam or CO₂ gasification agent provides a necessary reaction environment for the tar conversion, and ensure that catalytic deactivation of biochar cannot be caused by the carbon deposition of tar during the reaction process. The biochar catalytic activity in biomass tar reforming is significantly affected by the alkali and alkaline earth metallic (AAEM) species [7–9] in the biochar.

In the previous studies [10,11], the biomass pyrolysis volatile contains complex tar components. It is difficult to clearly explain the reaction path of the single tar component in the volatile-char interaction process. The specific reaction path and change law of single tar molecular can be directly studied by using the model

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tar compounds. As also, the experiment research is usually focused on the reforming process of the pyrolysis tar with char. It does not consider the effect of gasification agent on the char. In the real tar cracking process by biochars during gasification, the char will be gradually consumed by gasification agents, such as H₂O and CO₂. The catalytic reaction is a dynamic process. Therefore, in this paper, we studied the reforming process of tar model compounds, as well as the dynamic consumption of biochars by H₂O or CO₂.

Nowadays researches [12,13] are mainly based on the different pretreatments of biomass feedstock to study the influence of AAEM species on tar cracking with biochar. In fact, the presence of AAEM species in biomass would result in the difference of biochar structures during pyrolysis [12,14]. In order to avoid the influence of biochar structure on the tar reforming, the acid-washing and ion-exchanging were used to pretreat the pyrolysis biochar to investigate the dynamic catalytic activities of K and Ca in biochar for the model tar compounds reforming under H₂O or CO₂ atmosphere.

In order to characterize the mechanism during reaction, the AAEM species in biochar can be quantified using the inductively coupled plasma-atomic emission spectroscopy (ICP-AES) to investigate their loaded conditions and precipitation laws. The physico-chemical forms and properties of AAEM species in biochar would be determined by biochar structure to which AAEM species are bonded and with which AAEM species interact [15]. Numerous techniques can be applied to study changes in biochar structures. X-ray diffraction (XRD) is useful for characterizing crystalline structure [16]; however, biochars are highly disordered carbonaceous materials that have a short-range order polycrystalline structure. While Fourier transform infrared spectroscopy (FTIR) has been used to examine the O-containing functional groups in biochars [17,18], it is of limited use for less-polar aromatic structures and sp³-sp³ or sp³-sp² cross-linked structures. Raman spectroscopy [19–21], especially as for highly disordered carbonaceous materials [22–24], is an ideal technique to describe the structural features of biochars, because it is sensitive to both the crystalline and amorphous structures. The presence of a wide variety of aliphatic structures and O-containing structures in biochars for the model tar compounds reforming under H₂O or CO₂ means that the biochar will be distinctly different from the well-structured carbon materials and the Raman spectroscopic investigation would be the best option to get clear insight for those structures [25]. For the quantitative analysis of model tar compounds, the Gas Chromatograph-Mass Spectrometer computer (GC-MS) can provide sufficient data supports [26–28].

In this paper, the objectives are to understand the different selectivity of active sites on biochar, the transformation mechanism of biochar structures and the reaction route of tar catalytic reforming, all of which are essential to the catalytic elimination of biomass tar with pyrolysis biochar. Investigation of the catalytic reforming of model tar compounds with pyrolysis biochar under H₂O/CO₂, provides a solid theoretical foundation for the removal of real tar components during biomass thermal conversion. It could provide the selection of biochars with AAEM species and specific structures as active sites to be used in the subsequent biomass utilization. While making full use of the pyrolysis biochar products, the clean utilization of biomass is realized.

2. Experimental

2.1. Material preparation

Biomass (rice husks) obtained from the Wu Chang area in Harbin, Heilongjiang Province, China, was used in the experiments. The samples were dried overnight at 105 °C, pulverized, and sieved to obtain a fraction with particle sizes between 0.09 and 0.15 mm. The proximate and ultimate analyses data for the rice husks (0.09–0.15 mm fraction) are listed in Table 1.

Toluene, naphthalene and phenol were selected to represent the three main types of biomass gasification tar. Light tar compounds are converted faster than heavy tars, and these three tars represent the lightest compound in each family. Toluene is the lightest alkyl aromatic tar, naphthalene is the lightest PAHs, and phenol is the lightest heteroatom-containing compound [28]. The three tar compounds, i.e., toluene, naphthalene, and phenol (Guaranteed reagent, supplied from Harbin Zhongjia chemical reagent co., Ltd.), were pre-dissolved together to prepare the model tar compounds. According to the dissolution properties of the three kinds of tar samples by test and the tar concentration within the typical range for biomass gasification gas [28,29], the amounts of model tar compounds injected into the gas were adjusted to obtain a liquid mixture with the weight ratios of toluene:naphthalene:phenol = 5:2:1.

2.2. Catalyst preparation

The raw biochar samples were prepared from the pyrolysis of biomass samples. Pyrolysis had been carried out using a quartz one-stage reactor (as shown in Fig. 1) at a slow-heating rate of 10 °C/min and a final pyrolysis temperature of 800 °C with a hold-

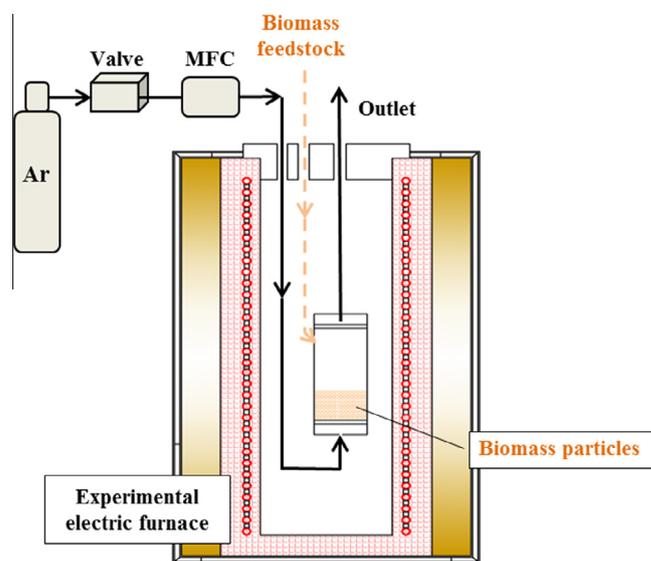


Fig. 1. Schematic diagram of one-stage reactor used for preparing raw biochars under Ar at 800 °C.

Table 1
Proximate and ultimate analyses of rice husk.

Proximate analysis				Ultimate analysis					Low heat value $Q_{net,ar}^C/(kJ \cdot kg^{-1})$
M_{ar}	A_{ar}	V_{ar}	FC_{ar}	C_{ar}	H_{ar}	$O_{ar,diff}$	N_{ar}	$S_{t,ar}$	
(wt%)	(wt%)	(wt%)	(wt%)	(wt%)	(wt%)	(wt%)	(wt%)	(wt%)	
10.50	16.34	58.53	14.63	35.89	4.23	32.72	0.19	0.13	12.80

Note: diff. = by difference, ar. = as received basis.

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