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Full Length Article

Catalytic mechanism of ion-exchanging alkali and alkaline earth metallic species on biochar reactivity during CO_2/H_2O gasification

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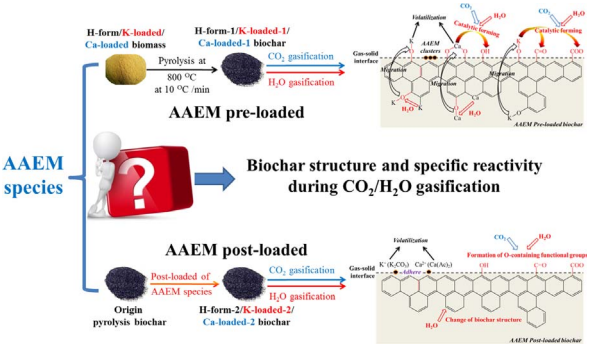
GRAPHICAL ABSTRACT



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ABSTRACT

To understand the detailed catalytic mechanism of ion-exchanging AAEM species on biochar structure and its specific reactivity during CO_2/H_2O gasification, the experiments were carried out in a laboratory fixed-bed reactor at 800 °C, with two kinds of AAEM-loading methods. The migration and precipitation characteristics of AAEM species was evaluated by ICP-AES, while the transformation of biochar structures were analyzed by FTIR and Raman. The specific reactivity of H_2O/CO_2 gasification biochar was determined by TGA analysis in Air at 370 °C. The results show that the stronger catalytic properties of K and Ca species in H_2O atmosphere are obtained than that in CO_2. The effect of K is mainly on the formation of O-containing functional groups (e.g. alcohol/phenolic-OH, aldehyde/ester C═O and carboxylic −COO− groups) and the transformation from small ring systems to larger ones, while the catalytic effect of Ca is only to increase the proportion of large aromatic ring structures (≥6 fused benzene rings). The biochar-CO_2 reaction took place mainly at the gas-solid interface of biochar, while biochar-H_2O one existed throughout the biochar particle. A better distribution of active sites (i.e. surface K/Ca species and O-containing groups) on biochar surface would result in the high specific reactivity of biochar during gasification.

1. Introduction

A sustainable energy future is looking forward all over the world, with the combination of factors such as renewable resources and advanced energy technology. Biomass is an abundant, clean and carbon-neutral renewable energy, exhibiting a great prospect to reduce the

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Table 1
Proximate and ultimate analyses of rice husk samples.

Sample	Proximate analysis (wt%)				Ultimate analysis (wt%)				
	Moisture $_{ad.}$	Ash$_{ad.}$	Volatiles $_{ad.}$	Fixed carbon $_{ad.}$	$C_{ad.}$	$H_{ad.}$	$O_{ad.(diff)}$	$N_{ad.}$	$S_{t,ad.}$
Rice husk	6.86	17.00	60.92	15.22	37.35	4.40	34.05	0.20	0.14

Note: diff. = by difference, ad. = air dry basis.

global environmental pollution and energy crisis. Gasification, with H_2O/CO_2 as the gasifier agent, is one of the effective thermochemical conversion processes for biomass energy [1], especially for the catalytic gasification [2], along with lower emissions of CO_2 and other gaseous pollutants. In a large amount of previous investigations [3–7], it can be seen that the alkali and alkaline earth metallic (AAEM) species, no matter inherent or ion-exchanged in biomass, played a significant catalytic role during the biomass thermal conversion. According to Shadman et al. [8], the catalytic role of AAEM species would be reflected in three important processes: (i) AAEM re-distribution on biochar surface by migration; (ii) loss of AAEM species by vaporization; and (iii) change of biochar structure due to carbon conversion.

Although the effect of AAEM species during biochar gasification has been studied to some extent [7,9–11], however, the detailed catalytic mechanisms of ion-exchanging K and Ca on biochar during H_2O/CO_2 gasification are not well understood yet. Walker and De Lecea [12,13] pointed out that the catalytic abilities of AAEM species were different during the gasification of biochar with H_2O and CO_2, due to the various mechanisms between H_2O/CO_2 and biochar. While, Meijer et al. [14] observed the result that the effect of K on the H_2O gasification is similar to that on CO_2 one. The AAEM species organically linked to the biomass through ion-exchanging would promote the biomass gasification to form the gas-liquid-solid products. The AAEM species during gasification mainly acted in the gasification primary stage, namely the decomposition/pyrolysis of biomass [15,16], which can play an important role in overall biomass gasification reactions. It can be described that the ion-exchanging AAEM species could enhance the secondary reforming/cracking of macromolecular compounds of volatiles produced from pyrolysis of biomass, and promote their polymerization reactions to form the biochar samples with more active physicochemical structures. According to Lang et al. [17], K would be mobile and distribute itself during the gasification, and Ca could also be well-dispersed in the sample and transferred to acid sites by ion-exchanging. Zolin et al. [18] indicated that the AAEM species in wheat straw would volatilize into the gas-phase products and participate in the H_2O gasification reactions of biochar. According to Jiang et al. [7], Ca would be with more strong effects on the water-gas-shift reaction ($CO + H_2O \leftrightarrow CO_2 + H_2$) of biochar than the K. According to Perander et al. [10], during the CO_2 gasification of biochar, the catalytic effect of Ca was higher than that of K at the early stage of gasification (Ca > K), but the decreasing of catalytic ability of Ca would be also faster than that of K.

In order to study the catalytic effect of ion-exchanging AAEM species on biochar gasification in detail, the methods of AAEM loading into the biochar seem to be significantly important. For such experiment results mentioned above, the biochar reactivity would be influenced by the ion-exchanging AAEM species, while the differences of biochar initial structures would play an important role during H_2O/CO_2 gasification [19]. Thus, according to Yip et al. [20], the AAEM species post-loaded into the pyrolysis biochar directly, instead of pre-loaded into the raw biomass, would be a better approach to investigated the effect of AAEM species as the single-factor on biomass gasification, with little differences in the biochar structure [21]. Wu et al. [22] indicated that the AAEM species loaded directly into char would behave quite differently from that in the char from the pyrolysis of AAEM pre-loaded raw sample. Nanou et al. [23] investigated the reactivity of biochar under gasification conditions, and indicated that pre-loading AAEMs in the wood before pyrolysis results in a better distribution of active sites than post-loading ones in the biochar (after pyrolysis). Yip et al. [20] applied the acid treatment of biochar after biomass pyrolysis, and indicated that K and Ca retained in biochar are the key catalytic species, with the catalytic effect of K > Ca during the H_2O gasification. Thus a good understanding of catalytic mechanism of ion-exchanging alkali and alkaline earth metallic species on biochar reactivity during CO_2/H_2O gasification is highly significant for developing gasification technology of biomass.

The main objectives of the study were: (1) to determine the migration and volatilization characteristics of AAEM species; (2) to study the impact of ion-exchanging K/Ca species on biochar structure and examine its catalytic mechanism; and (3) to explore the specific reactivity of H_2O/CO_2 gasification biochar catalyzed by AAEM species.

2. Material and methods

2.1. Material preparation

Rice husk, obtained from the Wu Chang area in Harbin, Heilongjiang Province, China, was used in the experiments. The biomass samples were dried overnight at 105 °C, pulverized and sieved to obtain particles in 0.15–0.25 mm. The proximate and ultimate analyses data for rice husk are listed in Table 1.

The pyrolysis biochar samples were prepared from 1.0 g rice husk (raw or AAEM pre-loaded) in Ar atmosphere, which was carried out in a fix-bed quartz reactor, as shown in Fig. 1 (a) and (b), at a slow-heating rate of 10 °C/min and a final pyrolysis temperature of 800 °C with a holding time of 10 min. After that, the reaction was quenched by removing the reactor from the furnace. The pyrolysis biochar was collected and stored in a freezer (about 4 °C) for the preparation of AAEM-loaded pyrolysis biochar and further H_2O/CO_2 gasification.

2.2. AAEM-loaded pyrolysis biochar preparation

The AAEM-loaded pyrolysis biochar samples were prepared in two ways. One was the “AAEM pre-loaded biochar”, formed from the direct pyrolysis of AAEM-loaded biomass feedstock [24,25], which were called as H-form-1, K-loaded-1 and Ca-loaded-1 biochar. Another one was the “AAEM post-loaded biochar” obtained by the AAEM loading of pyrolysis biochar from the raw biomass feedstock [20,23], which were termed as H-form-2, K-loaded-2 and Ca-loaded-2 biochar. As shown in Fig. 2, the specific experimental steps of the AAEM-loading method, using the aqueous solutions of 0.2 M H_2SO_4, K_2CO_3 and $Ca(CH_3COO)_2$, can be seen in our previous study [21]. The AAEM species content in the AAEM pre/post-loaded pyrolysis biochar can be seen in Table 2.

2.3. H_2O/CO_2 gasification of biochar

The fix-bed quartz reactor, as shown in Fig. 1 (b), was used for the H_2O/CO_2 gasification of AAEM pre-loaded (or post-loaded) pyrolysis biochar. About 0.5 g of H-form/K-loaded/Ca-loaded-1 (or -2) biochar samples were pre-loaded into the top stage of quartz reactor followed by argon purging of 1.8 L/min for 15 min and then heated to 800 °C with the heating rate of 10 °C/min. When the temperature stabilized at 800 °C, the atmosphere was switched to pure CO_2 or 15 vol% H_2O. The

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