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# Catalytic effects of inherent alkali and alkaline earth metallic species on steam gasification of biomass

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## ABSTRACT

This study aimed to understand the mechanism of dual catalytic effects of inherent alkali and alkaline earth metallic species (AAEMs) on biomass gasification. Two kinds of typical Chinese agricultural biomass were gasified using updraft quartz reactor with steam. The results indicated that external steam had negligible effects on promoting further thermal cracking or reforming of tar under 900 °C. The presence of AAEMs enhanced the production of H<sub>2</sub> and CO<sub>2</sub>, while inhibited the production of CO, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>. The heterogeneous char-steam reaction, as well as the homogeneous hydrocarbons reforming and water-gas shift reactions were promoted by the presence of AAEMs. Alkaline earth metals had more significant catalytic effects on water-gas shift reaction compared to alkali metals. The results from UV fluorescence spectra further proved that the additional steam had negligible promoting effects on secondary reforming of tar, while the inherent AAEMs had a significant catalytic role in thermal cracking and reforming of tars.

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## Introduction

lignocellulosic biomass, which is an abundant, clean and carbon-neutral renewable energy, exhibits great prospects of substituting for the use of fossil fuels to reduce global environmental pollution and energy crisis. Gasification is one of

the most efficient ways to utilize biomass, wherein, biomass is converted to fuel gas which is suitable for feeding gas turbines and gas engines as well as synthesis of bio-fuel [1]. In particular, steam gasification of biomass is remarkably attractive due to its high hydrogen yield. The principal reactions in steam gasification of biomass are as follows [2,3]:

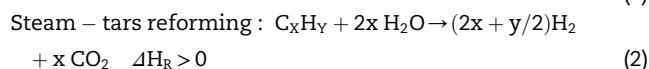
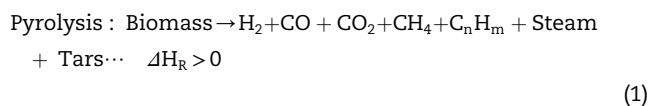
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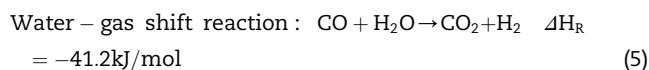
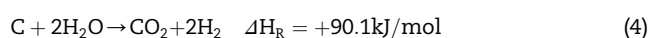
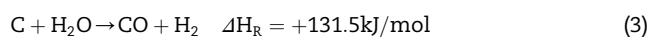
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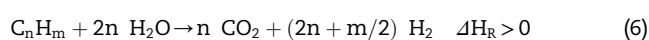
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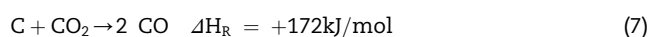
where C<sub>x</sub>H<sub>y</sub> represents large condensable hydrocarbons (or tars)Char gasifications:



Hydrocarbon reforming:



where C<sub>n</sub>H<sub>m</sub> represents light non condensable gases such CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> etc.Boudouard reaction:



Compared to the coal, one of the significant differences of lignocellulosic biomass is that the considerable amounts of AAEMs such as potassium, sodium, calcium, magnesium etc were contained [4–7]. Many researchers [8–11] have found that the AAEMs in biomass feedstock play catalytic role during biomass thermal conversion, and the high contents of AAEMs are prone to volatilize as gaseous phase and also be involved in the steam reforming reactions [12]. Biomass gasification process is possible to be significantly altered via the catalytic alteration of above reaction pathways by AAEMs. Thus a good understanding of catalytic role of AAEMs in steam reforming process of biomass is highly significant for developing gasification technology of biomass.

A quick review of the published reports [13–17] shows that the major share of interest is mainly focused on performance of various externally added catalysts during steam gasification of biomass. Zhang et al. [13] studied the added potassium catalysts in steam gasification of tobacco stalk sample. They found from 600 °C to 700 °C, the addition of K<sub>2</sub>CO<sub>3</sub> or CH<sub>3</sub>COOK catalysed the gasification for hydrogen production, and hydrogen yield and carbon conversion increased with increased their catalyst loadings. However, the hydrogen yield and carbon conversion decreased as increased the amount of KCl due to inhibition of KCl on gasification. Waheed et al. [14] investigated hydrogen production from the catalytic steam gasification of bio-char derived from the pyrolysis of sugar cane bagasse. They found the hydrogen yield in the absence of a catalyst at 950 °C was 100.97 mmol g<sup>-1</sup>, the presence of the Ni–MgO and Ni–Al<sub>2</sub>O<sub>3</sub> catalysts produced significantly improved hydrogen yields of 178.75 and 187.25 mmol g<sup>-1</sup> respectively at 950 °C. The hydrogen yield from the char with the Ni-dolomite only showed a modest increase in hydrogen yield. Wang et al. [16] conducted steam gasification of biomass using Co/Mg/Al catalysts. They found the Co/Mg/Al (10/40/50%) catalyst exhibited much higher activity and resistance to coke deposition.

However, only a few studies about the catalytic performance of inherent ash-forming AAEMs for steam reforming of biomass could be found. It is possible that inherent ash-forming AAEMs which are rich in biomass feedstock could be an available catalyst for steam gasification of biomass. Hauserman [18] studied the catalytic effects of gasified wood ash during gasification of biomass and coal. They found the wood ash was mainly composed of 44.3 wt% CaO, 15.3 wt% MgO and 14.5 wt% K<sub>2</sub>O, and at 750 °C gasification temperature, the reactivity of bituminous coal and wood increased 21.5 and 30 times respectively when separately adding 20 wt% and 10 wt% wood ash. They pointed out wood ash was a possible catalyst for the gasification reaction. Nanou et al. [19] studied the influence of ash which was specific ash components or derived from pine wood on the steam gasification rate of pine wood char. They found impregnation of ash/ash components by ~10 wt% or more resulted in a significant increase in the gasification rate, and the char was feasible to be catalysed by concentrating the ashes during steam gasification reaction. Skoulou et al. [20] studied effect of biomass water leaching on H<sub>2</sub> production and tar steam reforming. They found water leaching did not favour tar steam reforming, while at the same time decreased H<sub>2</sub> yield in gas product under air gasification conditions, due to possible loss of the catalytic effect of ash with water leaching. The above literature review suggests there are few systematic scientific works related to catalytic behaviour of inherent AAEMs during steam gasification of agricultural biomass.

Additionally, biomass demineralization has been proved as an available method to study the minerals catalytic effects on biomass thermal conversion by removing them from biomass. Moreover, our previous work [21] indicated the inherent alkali metals (K, Na) and alkaline earth metals (Ca, Mg) of rice straw could be respectively removed by water and HCl solution, thus water and HCl leaching maybe a good way to separately evaluate the catalytic effects of inherent alkali metals and alkaline earth metals of lignocellulosic biomass.

Therefore, this study aimed to systematically investigate the catalytic effects of inherent AAEMs on yield and composition evolution of tar and syngas during steam gasification of biomass by using washing method to unravel the catalytic mechanism of inherent AAEMs.

In this study, two kinds of typical Chinese agricultural residues were chosen as the feedstock due to its abundance in China and other Asian countries, as well as high content of AAEMs. Rice straw and rice husk were respectively washed by water and HCl solution which gave a chance to separately investigate catalytic effects of inherent alkali metals (K, Na) and alkaline earth metals (Ca, Mg) on steam gasification of biomass. The yield and composition of syngas with/without washing treatment were determined by gas chromatography (GC). The composition and aromatic ring structure evolution of the tars were respectively analysed by gas chromatography–mass spectrometry (GC–MS) and ultraviolet fluorescence spectroscopy (UV-F). Finally, the catalytic behaviour of inherent alkali metals and alkaline earth metals on steam gasification of biomass was determined.

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