Biomass and Bioenergy 107 (2017) 261–270

Contents lists available at ScienceDirect

Biomass and Bioenergy

journal homepage: www.elsevier.com/locate/biombioe

Research paper

In-situ steam reforming of biomass tar over sawdust biochar in mild catalytic temperature

Dongdong Feng[a], Yijun Zhao[a,*], Yu Zhang[a,b,**], Zhibo Zhang[a], Linyao Zhang[a], Shaozeng Sun[a]

[a] School of Energy Science and Engineering, Harbin Institute of Technology, Harbin, 150001, China
[b] Faculty of Engineering, University of Nottingham, Nottingham, NG7 2TU, UK

ARTICLE INFO

Keywords:
In-situ
Mild temperature
Tar reforming
Steam
Biomass tar
Sawdust biochar

ABSTRACT

In order to fully understand the catalytic activities of sawdust biochar on in-situ tar steam reforming in mild catalysis temperatures (650–800 °C), the experiment was carried out in a two-stage fluidized bed/fixed bed reactor. The structural characteristics of biochar were analyzed by the Raman and XPS spectroscopies. The results of in-situ tar steam reforming over biochar were performed by gas chromatograph/mass spectrometer (GC/MS). Kinetic aspects of tar steam reforming in mild temperatures were calculated to evaluate the catalytic effect of sawdust biochar on in-situ tar reforming. The results indicate that sawdust biochar has a positive effect on in-situ tar steam reforming, while the effect is not proportional to biochar amount. During the in-situ tar steam reforming over biochar, the changes of oxygen-containing functional groups on biochar surface are mainly caused by the C-O bonds. The first order kinetic rate constant of sawdust biochar for the heterogeneous reforming of biomass tar at 650–800 °C is found to have an apparent activation energy (E_{app}) of 35.03 kJ/mol with the apparent pre-exponential factor (k_{app}) of 1.8×10^4 m^3 $kg^{-1}h^{-1}$. The biochar structures were considerably transformed during the tar steam reforming. According to GC/MS analysis of biomass tar, the biochar seems to promote the cracking of large ring polyaromatic tar compounds to form 1-ring aromatic ones.

1. Introduction

Biomass is a source of abundant, environmentally friendly, and renewable energy, and it may be an ideal alternative to fossil fuels for hydrogen and syngas [1–5]. One of the major challenges for the commercialization of biomass gasification is to find an economic and effective way to eliminate the biomass tar in the product gas [6,7]. Among the several methods for tar elimination, the physical treatment [8,9] usually wastes too much washing water and other natural material, the thermal cracking [10,11] needs to consume too much energy for tar transformation. Thus the catalytic reforming [12–14] seems to be the most attractive technology in large-scale applications due to its fast reaction rate, high reliability, and increase the quantity of usable gases. As steam can participate in various reactions such as the reforming of tar/gaseous hydrocarbons, water-gas shift reactions and biomass gasification, the tar steam catalytic reforming [6,13,15–18] attracts a lot of attention all over the world.

As a promising alternative, the catalytic activity of biochar has been compared with other conventional catalysts for tar reduction and the in-situ cracking of tar compounds [19]. It was found that biochar is a promising catalyst for solving the tar utilization problems in gasification systems [19–21] and there is requirement to perform more experimental studies in this direction. El-Rub et al. [19] investigated the biochar as an in-situ catalyst for tar removal in gasification systems in a fixed bed reactor and indicated the real tar was realized almost complete conversions at temperatures ≥ 800 °C. Yao et al. [22,23] studied the in-situ destruction of nascent tar over biochar and indicated that the biochar has a positive effect on tar destruction in steam at 850 °C. Yi et al. [24] also made an investigation on tar destruction over biochar in a lab-scale two-stage reactor at up to 1000 °C. Most relevant investigations were concentrated on the tar reforming over a fixed amount of biochar samples in high temperatures (mainly above 800 °C). In recent years, the gasification technology in mild temperatures (< 800 °C) has potential applications in sustainable development biomass because it is thermally and economically efficient [25]. Lowering the gasification temperature is an effective method for preventing agglomeration and ensuring good fluidization [26], more importantly, improving the system efficiency [27]. However, a comprehensive study of in-situ tar steam reforming over biochar in mild temperatures is not found. Therefore, in the mild catalytic temperature conditions, the

* Corresponding author.
** Corresponding author. School of Energy Science and Engineering, Harbin Institute of Technology, Harbin, 150001, China.
E-mail addresses: 08031175@163.com (D. Feng), zhaoyijun@hit.edu.cn (Y. Zhao), 759658674@qq.com (Y. Zhang), 1071418610@qq.com (Z. Zhang), 1206780473@qq.com (L. Zhang), sunsz@hit.edu.cn (S. Sun).

http://dx.doi.org/10.1016/j.biombioe.2017.10.007
Received 8 April 2017; Received in revised form 8 October 2017; Accepted 13 October 2017
0961-9534/

mechanism of tar steam reforming over biochar during biomass gasification is urgent to be investigated.

Among the complex characteristics of biochar which are used for the in-situ tar steam reforming, the investigation of specific effects of different amounts of biochar on tar reforming could make a solid foundation for the innovative application of biomass char for in-situ tar removal in a biomass gasifier, which is rare indicated in precious literature [28,29]. In addition, compared with the extensive research of inherent/loaded metal elements (e.g. alkali and alkaline earth metallic species) on the reactivity of biochar for tar reforming [30–35], the effect of biochar structure has not been clearly discussed, not even to mention the conditions over different amounts of biochar in mild temperatures. The biochar structural features such as the O-containing groups on the char surface are an important factor influencing the tar destruction [22,23]. Min et al. [36] provided insights to the changes in char structure as well as the importance of alkali and alkaline earth metallic (AAEM) species during tar reforming, while Asadullah et al. [37] suggested that the structure of biochar played a more dominant role than the catalytic effects of AAEM species in the char reactivity. It is necessary to fully investigate the transforming mechanism of biochar structure during in-situ tar steam reforming over biochar, which can provide the guidance on the specific reforming pathway of biomass tar in biochar.

The main objective of this paper is to study the catalytic behavior of in-situ biomass tar steam reforming over different amounts of sawdust biochar in mild catalysis temperatures. The in-situ biomass tar steam reforming over biochar was investigated in a two-stage fluidized bed/fixed bed reactor. The characteristics of biochar and biomass tar were studied by Raman, XPS and GC/MS, respectively. The experiment would provide some guides for the clean utilization of biomass gasification technology in the moderate temperatures.

2. Experiment

2.1. Material preparation

Sawdust obtained from the northeast of China, were used to prepare the biochar catalyst for in-situ biomass tar H_2O reforming. The samples were dried at 105 °C, pulverized to particles with the size of 0.15–0.25 mm. The rice husk was washed with 0.2 M H_2SO_4 solution to remove the inherent metallic species. The acid-washed rice husk (0.15–0.25 mm) was used to supply the in-situ biomass tar. The proximate and ultimate analyses data for the sawdust and rice husk are listed in Table 1.

The sawdust biochar was prepared in a quartz fixed-bed reactor, as shown in Fig. 1. 5.0 g samples were uniformly placed in the quartz reactor. Pyrolysis had been carried out in 2.0 L/min Ar atmosphere at a slow-heating rate of 10 °C/min and a final pyrolysis temperature of 800 °C. The pyrolysis residence time for biochar preparation was 30 min to ensure the sawdust was completely decomposed and no secondary cracking would occur in the following tar reforming process. The primary metal analysis of sawdust biochar is listed in Table 2.

Table 1
Proximate and ultimate analyses of rice husk and sawdust.

Samples	Proximate analysis (*wt*%)			Ultimate analysis (*wt*%)				
	$V_{d.}$	$FC_{d.}$	$A_{d.}$	$C_{d.}$	$H_{d.}$	$O_{d.(diff.)}$	$N_{d.}$	$S_{t,d.}$
Rice husk	65.41	16.34	18.25	40.10	4.72	36.56	0.21	0.15
Sawdust	85.22	13.72	1.06	48.30	5.87	44.62	0.13	0.01

Note: diff. = by difference, d. = dry basis.

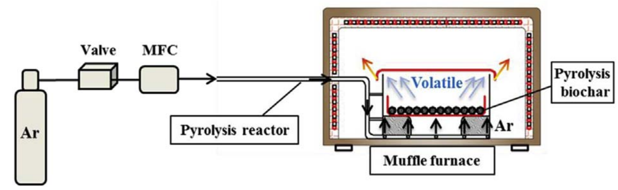

Fig. 1. Sawdust catalyst preparation system.

Table 2
Primary metal contents of sawdust biochar.

Sample	Metallic species analysis (*wt*.%)					
	Na_2O	K_2O	MgO	CaO	Fe_2O_3	Al_2O_3
Sawdust biochar	0.038	0.445	0.149	1.269	0.083	0.184

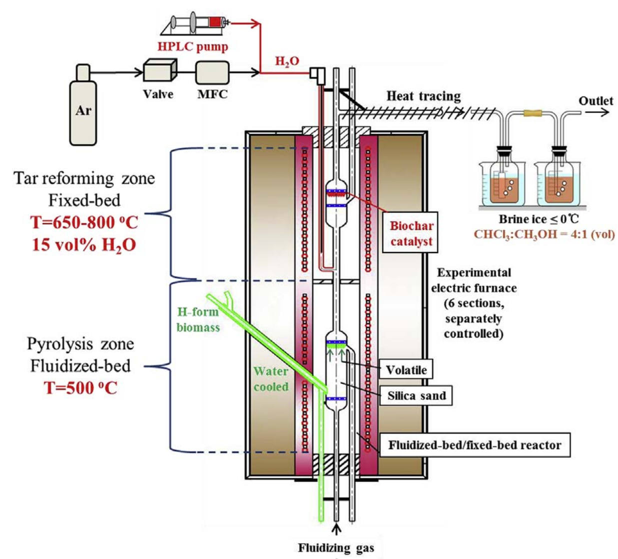

Fig. 2. Schematic diagram of fluidized bed/fixed bed reactor for in-situ tar steam reforming with biochar.

2.2. In-situ biomass tar steam reforming over biochar

The in-situ biomass tar steam reforming over biochar was investigated in a two-stage fluidized bed/fixed bed reactor, as shown in Fig. 2. The system was heated to 500 °C at the bottom stage (fluidized bed) and 650–800 °C at the top stage (fixed bed). Different amounts of sawdust biochar (0.2/0.5/1.0 g) were pre-loaded into the fixed bed stage, with the tar homogeneous reforming reaction without biochar catalyst as the blank experiment. The silica sand was used as bed material in the fluidized bed stage. The acid-washed rice husk was entrained into the fluidized-bed at 100 mg/min via a water-cooled probe. The biomass tar from rice husk pyrolysis was carried directly through the fixed-bed stage for in-situ tar steam reforming over biochar. At the same time, the atmosphere was switched into 15 *vol*.% steam, which was achieved by feeding liquid-water directly into the heated reactor by a high performance liguid chromatography (HPLC) pump. The carrier Ar gas (> 99.999%) of feeding system was fixed at 1.0 L/min and the amount of fluidizing gas was 1.50 L/min. In order to ensure the residence time unchanged during biomass tar passing through biochar at 650–800 °C, the deionized water were given with the balanced Ar gases, as shown in Table 3. After reaction, the biochar samples were collected and stored in a freezer at 4 °C.