INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2017) 1–9

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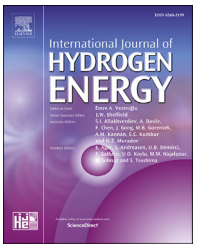

Co-processing methanol and ethanol in bio-char steam gasification for hydrogen-rich gas production

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ARTICLE INFO

Article history:
Received 20 February 2017
Received in revised form
15 April 2017
Accepted 2 May 2017
Available online xxx

Keywords:
Bio-char
Hydrogen
Steam gasification
Additives

ABSTRACT

Co-processing methanol and ethanol in bio-char steam gasification was investigated in a fixed-bed reactor. The effect of reaction temperature, steam flow rate and additives content on gas composition and H_2 yield were evaluated. The results showed that bio-char is an ideal material for H_2 production, and the maximum H_2 yield (233.3 g/kg bio-char) was obtained in the absence of additives at 950 °C, 0.5 g/min steam flow rate, meantime, producing hydrogen-rich gas with slight formation of methane. Methanol and ethanol blended with steam, and subsequently introduced in reactor have positive effect on H_2 yield. However, taking the economy and char conversion rate into consideration, 5 vol%–8 vol% may be suitable contents, and H_2 yield increased to 342 g/kg and 308.9 g/kg with 5 vol% of methanol and ethanol added in gasifying agent at 950 °C and 0.5 g/min steam flow rate. Furthermore, the proposed catalytic gasification of hydrogen-rich gas for high purity hydrogen and synthetic natural gas may be a promising way for using the produced gases.

Introduction

Hydrogen as a pollution-free and highly efficient energy carrier has widespread applied in internal combustion engines and fuel cells, as well as chemical industry (i.e. oil refining and ammonia manufacturing), and is considered to be an ideal alternative energy [1,2]. Currently, fossil fuels are mainly sources for producing hydrogen in industrial scale due to the limitations of technology and economy. Especially, steam reforming of natural gas contributes the most employed process [3,4]. Taking the gradually depletion of fossil fuels and contamination into consideration, it is clearly not sustainable and environmentally friendly routes. Renewable sources such as biomass should be used to produce hydrogen. Biomass is an abundant and especially CO_2 neutral resource through photosynthesis of green plants, which makes it a potential substitute for fossil fuels [5].

Nowadays, Pyrolysis, gasification and liquefaction are available thermo-chemical technologies for conversion biomass efficiently. Among these methods, steam gasification of biomass has been proved as an attractive process for producing hydrogen-rich gas [6]. However, the process

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http://dx.doi.org/10.1016/j.ijhydene.2017.05.008

unavoidably suffers from the non-desirable byproducts of bio-oil and bio-char. As a result, several technical problems such as catalyst deactivation, fouling and plugging pipelines may be caused by the condensed tar. Numerous attempts have been tried to remove tar from the raw gas [7]. But, completely destructing the tar for relatively tar-free gas rich in hydrogen has never been observed in large scale. Consequently, in order to avoid the influence of tar, many researchers have focus on bio-char steam gasification. Waheed et al. [8] studied the high temperature steam gasification of bio-char from sugar cane bagasse. They suggested that char steam gasification is a promising way for hydrogen production. Gai et al. [9] pre-treated sewage sludge via hydrothermal carbonization with the steam gasification in fixed-bed reactor. The results showed that high hydrogen yield and energy efficiency can be obtained compared with steam gasification of sewage sludge under same conditions. Gai et al. [10] obtained similar results by steam gasification of hydrochar derived from sewage sludge. Compared with raw biomass material, lower contents of volatile and oxygen are observed in char. Therefore, introducing steam as gasifying agent into char gasification process not only boost hydrogen and gas yield, but also achieve high quality of raw gas.

Additionally, co-gasification of different mixtures can be an alternative to single material steam gasification since it has received great concerns in recent years. As a combined strategy, co-gasification of different materials has regarded as a higher energy conversion efficiency, operation stability and economic advantages process. But, a huge amount of studies focused on co-gasification of blends of two solid fuels with different characteristics [11,12] or mixtures of biomass and liquid fuels such as crude glycerol [13]. Lopez et al. [14] used a conical spouted bed reactor for steam gasification of forest pinewood waste and high density polyethylene blends at 900 °C using olivine to crack tar. There had a positive synergetic effect under the addition of plastic involving the reduction of tar and char contents, and also obtained high content of hydrogen in syngas. Skoulou and Zabaniotou [13] obtained similar results for gasification of crude glycerol and olive kernel blends. Furthermore, some researchers have considered co-processing methane or natural gas in high temperature steam gasification with biomass to increase the hydrogen yield in syngas or to boost the combustion characteristics [15,16]. However, there are no researchers adding additives in gasifying agent for improving the quality of syngas.

From reported literature, methanol and ethanol have been confirmed the potential for hydrogen production by steam reforming. Methanol reforming can be processed with a low reaction temperature. Therefore, several researchers have investigated methanol reforming for hydrogen production, which can be applied in fuel cells [17]. And in the works of Yan et al. and Majidi et al. [18,19], directly methanol fuel cell was performed with higher efficiency. Ethanol, as a less toxic and relatively high hydrogen content source, which can be produced from renewable biomass resources. Thus, steam reforming ethanol for hydrogen is regarded an attractive route. Lysikov et al. [20] studied ethanol reforming for high-purity hydrogen over the blends of commercial Ni based catalyst and sorbent CaO. The same occurs with the work done by Wu et al. [21].

The obvious advantages of methanol and ethanol are low steam reforming temperature and good miscibility with water, which can be co-processed simultaneously with bio-char steam gasification. Furthermore, heterogeneous reactions of char gasification are well known to be the limiting step in fluidized bed under the typical operational conditions. Thus, in the present work, co-processing methanol and ethanol in bio-char steam gasification for hydrogen-rich gas production was carried out in a fixed-bed gasifier. Effect of reaction temperature and steam flow rate on gas composition and H_2 yield of bio-char steam gasification was investigated. Because of the high temperature of bio-char steam gasification, it can supply sufficient heat for methanol or ethanol reforming. Thus, co-processing is a feasible way to improve hydrogen yield in syngas. And the effect of additives contents in the blends on gasification performances was reported. This may be available pathway for hydrogen production.

Material and methods

Materials

Bio-char was obtained from gasification residues of pinewood in a fluidized bed at a factory in Jiangsu province, China. Sample was pulverized and sieved into a specific particle size below 0.56 mm. The proximate and ultimate analysis of the bio-char is given in Table 1. The higher heating value (HHV) of the sample was calculated according to the Eq. (1) based on the elemental composition of feedstock [22]. The ultimate analysis was conducted using Vario Micro Cube Element Analyzer. The solutions of methanol (analytic reagent grade) and ethanol (analytic reagent grade) were prepared in different volume concentration.

$$\mathrm{HHV} = (349.1\mathrm{C} + 1178.3\mathrm{H} + 100.5\mathrm{S} - 103.4\mathrm{O} - 15.1\mathrm{N} - 21.1\mathrm{ASH})/1000 \ \mathrm{MJ/kg} \quad (1)$$

Experimental apparatus and procedure

The gasification experiments were investigated with a fixed-bed reactor of quartz tube placed in an electric furnace. A schematic diagram of fixed-bed system is shown in Fig. 1. The reactor is in length of 840 mm and an inner diameter of 55 mm, and the heating zone length is 400 mm. The

Table 1 – Proximate and ultimate analysis of bio-char.

	Bio-char
Proximate analysis (wt.%, dry basis)	
Volatile matter	9.7
Fixed carbon	84.1
Ash	6.24
Ultimate analysis (wt.%, dry ash free basis)	
C	87.1
H	1.9
N	0.8
S	0
O	10.2
HHV (MJ/kg)	29.4

Please cite this article in press as: Jia S, et al., Co-processing methanol and ethanol in bio-char steam gasification for hydrogen-rich gas production, International Journal of Hydrogen Energy (2017), http://dx.doi.org/10.1016/j.ijhydene.2017.05.008