Bioresource Technology 216 (2016) 159–164

Contents lists available at ScienceDirect

Bioresource Technology

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

Hydrogen production from biomass gasification using biochar as a catalyst/support

Dingding Yao [a], Qiang Hu [a], Daqian Wang [a], Haiping Yang [a,*], Chunfei Wu [b], Xianhua Wang [a], Hanping Chen [a]

[a] *State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, Wuhan 430074, China*
[b] *School of Engineering, The University of Hull, Hull HU6 7RX, UK*

HIGHLIGHTS

- Biochar showed a promising catalyst/support for biomass gasification.
- Interaction between Ni, biochar and volatiles was studied.
- Alkali and alkaline earth metals enhanced hydrogen production.
- Ni/CC exhibited the highest activity of H_2 production (92.08 mg g^{-1} biomass).

ARTICLE INFO

Article history:
Received 18 February 2016
Received in revised form 3 May 2016
Accepted 5 May 2016
Available online 11 May 2016

Keywords:
Biomass gasification
Biochar
Ni
Interaction
H_2

ABSTRACT

Biochar is a promising catalyst/support for biomass gasification. Hydrogen production from biomass steam gasification with biochar or Ni-based biochar has been investigated using a two stage fixed bed reactor. Commercial activated carbon was also studied as a comparison. Catalyst was prepared with an impregnation method and characterized by X-ray diffraction, specific surface and porosity analysis, X-ray fluorescence and scanning electron micrograph. The effects of gasification temperature, steam to biomass ratio, Ni loading and bio-char properties on catalyst activity in terms of hydrogen production were explored. The Ni/AC catalyst showed the best performance at gasification temperature of 800 °C, S/B = 4, Ni loading of 15 wt.%. Texture and composition characterization of the catalysts suggested the interaction between volatiles and biochar promoted the reforming of pyrolysis volatiles. Cotton-char supported Ni exhibited the highest activity of H_2 production (64.02 vol.%, 92.08 mg g^{-1} biomass) from biomass gasification, while rice-char showed the lowest H_2 production.

1. Introduction

The use of fossil fuels for energy and chemicals has significant challenges, considering the storage and environmental constrains (Sharma et al., 2015). The negative impacts of using fossil fuels have accelerated the exploration of renewable resources such as biomass, which can provide many kinds of sustainable and valuable fuels (Chen et al., 2014; Yang et al., 2016). Thermo-chemical treatment such as pyrolysis and gasification is one of the most promising methods for the utilization of biomass.

Hydrogen rich gas can be produced from biomass gasification using steam as gasifying agent. Up to 60–70 vol.% of H_2 concentration has been achieved in bench-scale fixed bed (Liu et al., 2014; Tang et al., 2015) and pilot scale fluidized bed (Fremaux et al., 2015) in the presence of catalyst. Catalyst plays an important role to enhance hydrogen production from biomass gasification. Among them, Ni-based catalyst is attractive, as it can reduce tar content and increase hydrogen production during biomass gasification, due to its good catalytic performance and relatively low cost (Wu and Williams, 2011; Zhao et al., 2015). Al_2O_3 is commonly used as catalyst support due to its physicochemical stability and excellent mechanical properties (Wu and Williams, 2009).

However, a significant problem of using Ni/Al_2O_3 is the catalyst deactivation caused by coke deposition on the surface of catalyst. Promoters such as Li, Na, Ca have been introduced into the Ni-based catalyst, as these promoters can activate H_2O to generate O^{2-} that is efficient to reduce coke formation (Srinakruang et al., 2005; Weerachanchai et al., 2009).

---

* Corresponding author.
E-mail address: yhping2002@163.com (H. Yang).

http://dx.doi.org/10.1016/j.biortech.2016.05.011
0960-8524/© 2016 Elsevier Ltd. All rights reserved.

It is known that some metals such as K and Ca are existed inside the biomass material. After pyrolysis, the contents of these metals are concentrated in the bio-char (pyrolysis residue). Some of these metals such as alkaline and alkaline earth metals (AAEMs) have been suggested to enhance the decomposition of hydrocarbons and water gas shift reaction during biomass reforming process (Hu et al., 2015; Shen and Yoshikawa, 2014). It is therefore interesting to apply bio-char as a primary catalyst to enhance the thermo-chemical conversion of biomass. In addition, some oxygen-containing functional groups presented in biochar have been reported to facilitate the decomposition of hydrocarbon volatiles (Shen, 2015; Song et al., 2014). Yan et al. (2010) and Sattar et al. (2014) studied the gasification of different bio-chars in a fixed bed reactor, suggesting that bio-char was an effective material for enhancing hydrogen-enrich gas production under optimal process conditions (e.g. temperature and steam content). Krerkkaiwan et al. (2015) reported the promising catalytic effect of biochar containing AAEMs for the reduction of tar derived from biomass gasification.

The combination of Ni and bio-chars were therefore suggested for hydrogen production from biomass gasification. Xiao et al. (2013) explored the gasification of waste biomass using a Ni/coal-char catalyst; a high H_2 yield of 25 mmol g^{-1} biomass was obtained at the optimum operation conditions. NiO mechanically mixed with wood-char and coal-char were prepared for the cleanup of biomass gasification syngas; more than 97% of tars removal efficiency had been achieved (Wang et al., 2011). Ni supported on biochar with different granular sizes were studied by Wang (2013); a middle size catalyst of 50–60 mesh were observed to result in the best performance in relation to the production of syngas and the removal of tar.

To our best knowledge, there are few studies investigating biochars produced from pyrolysis of different biomass samples for hydrogen production. It is reported that the composition, morphology and structure of biochars depended on the biomass feedstock (Liu et al., 2015). In addition, it is essential to understand the relationship between catalytic effect of biochar and its consumption (char gasification) during the process of hydrogen production from biomass gasification. The novelty of this work also includes the investigation of loading active Ni sites on biochars, produced from pyrolysis of wheat straw, rice husk and cotton stalk. These are common biomass feedstocks in China.

This work aims to enhance hydrogen production from biomass gasification using Ni-based catalyst with biochar as support. Interactions between metal, char and vapors from biomass pyrolysis will be particularly studied for fundamental understanding of the performance of the catalyst. The experimental work was carried out using a fixed two-stage reaction system for hydrogen production from biomass gasification.

2. Materials and methods

2.1. Experimental materials

The biomass material used in this research was wheat straw, with particle size between 100 and 200 μm. Three bio-chars, assigned as WC, RC, CC, were obtained from fast pyrolysis of wheat straw, rice husk and cotton stalk, respectively, in a lab-scale tube furnace at 500 °C. The bio-chars were used as catalyst supports. Commercial active carbon (AC) was also applied for the controlled trial.

It is noted that three biomass samples including wheat straw, rice husk and cotton stalk were used to prepare bio-chars, and one of the biomass sample (wheat straw) was also used as the raw material for hydrogen production from gasification process. The results of proximate and ultimate analysis of the three biomass samples are summarized in Table 1. X-ray fluorescence (XRF) analysis of the bio-chars are shown in Table S1. It shows that all the biomass are representative agricultural crops with low N and S content (<1 wt.%), representing clear raw resources. Table S1 shows the bio-chars contain large amount of Si, K and Ca metals. In particular, there is higher than 30 wt.% Si inside both WC and RC samples, about 19.0 wt.% K in the WC sample and around 15.85 wt.% Ca in the CC char sample.

2.2. Experimental setup and method

The pyrolysis–gasification process of biomass was conducted in a two-stage fixed bed reactor (Fig. S1), as mentioned in our previous paper (Yao et al., 2014). The reaction system consists essentially of a quartz tube gasification reactor (I.D. 51 mm) with two temperature ranges (Zone I: pyrolysis zone 310 mm height; Zone II: gasification zone, 310 mm height), a continuous feeding system, gas condensing system with ice and water mixture and a gas cleaning section followed by gas-sampling and measurement system.

Before each experiment, 0.85 g char with or without 0.15 g Ni was loaded in the middle of zone II, and a quartz basket with 1 g biomass was hold in the top of the reactor. High-purity nitrogen (99.99%) was supplied as carrier gas at 150 ml min^{-1}, also preventing the catalyst from oxidation. The reactor zone I was set at 500 °C for biomass pyrolysis, while the gasification temperature (T2) of zone II was set ranging from 600 to 900 °C with a 100 °C gap. After the reactor was heated up to the preset temperature and kept stable, the basket containing biomass sample was introduced into the middle of zone I. Biomass was promptly decomposed to form volatiles, undergoing catalytic reforming. Gas hourly space velocity (GHSV) was varied from 5000 to 7500 h^{-1} depending on the catalyst used (with or without Ni). After pyrolysis and catalytic reforming, the gas product was passed through a two-stage ice-water condenser for to collect condensable vapors. The non-condensable gases were periodically sampled with a 5 L gas bag. Experiments were repeated at least twice to ensure the reliability of the results.

The concentration of gas product (H_2, CO_2, CO, CH_4, N_2) was measured using a gas chromatograph (GC) (Micro-GC 9790II, Fuli Corp., China) equipped with a thermal conductivity detectors (TCD). The yield of each gas (H_2, CO, CH_4, CO_2) is quantified by:

$$\mathrm{H_2(CO,CH_4,CO_2)\ yield\ (mg{,}g^{-1}\ biomass)} = \frac{\text{mass of } \mathrm{H_2(CO,CH_4,CO_2)} \text{ obtained}}{\text{biomass mass in the feed}}$$

And the total gas yield was calculated as the sum of them. The liquid yield was obtained as:

$$\text{Liquid yield (wt.\%)} = \frac{W_t - W_0}{W_f} \times 100$$

where W_0 and W_t is the mass of condenser and pipeline before and after each experiment, and W_f means the total mass of feed (biomass and steam).

2.3. Catalyst preparation and characterization

Ni-based catalysts were prepared with an impregnation method. 10 g char was impregnated with an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$, then the precursors were stirred for 4 h and dried at 105 °C overnight, followed by the calcination under N_2 atmosphere at 800 °C. The Ni-based catalyst using activated carbon as support was denoted as Ni/AC. The loading of Ni of the Ni/AC catalyst was 5, 10, 15, 20 wt.%, respectively. 15 wt.% of Ni was loaded on the bio-chars (WC, RC and CC) produced from for Ni based

Table 1
Proximate analysis and ultimate analysis of biomass.

Biomass	Proximate analysis, d %			Ultimate analysis, d %					HHV d MJ/kg
	V	A	FC	C	H	N	S	O*	
Wheat straw	66.04	15.95	18.01	39.39	5.36	0.87	0.29	38.14	16.81
Cotton stalk	78.62	2.72	18.67	44.29	5.66	0.65	0.20	46.49	17.78
Rice husk	67.69	16.21	16.10	41.76	5.34	0.30	0.08	36.30	16.16

* was calculated by difference.

biochar. And the catalysts were denoted as Ni/WC, Ni/RC and Ni/CC, respectively. The catalysts were crushed and sieved to a particle size between 100 and 200 μm.

Quantification of inorganic species in bio-char samples was conducted by XRF (EAGLE III, EDAX Inc., USA). The surface area and pore structure of the chars and Ni-based catalysts were determined from N_2 adsorption isotherms operated at 77 K using automatic adsorption equipment (ASAP2020, Micromeritics, USA). Species identification of the fresh and reacted catalyst was performed with a X-ray diffraction (XRD) analyzer (X'Pert PRO, PANalytical B.V., Netherlands), with peaks being identified using High Score Plus software package. The measurement was completed in the 2θ range from 5° to 85° with a scan step size of 0.026°. Scanning electron micrograph (SEM) (JSM-5610LV, JEOL, Japan) operating at 20 kV was carried out to observe the morphology of carbon deposited on the catalyst, while surface elemental analysis of samples was conducted by energy dispersive X-ray spectroscopy (EDX).

3. Results and discussion

The process of biomass steam gasification can be divided into two main stages: (1) pyrolysis stage, where biomass is decomposed into char, volatiles and gases; and (2) reforming stage where volatiles/gases were reformed to produce gases like CO and H_2 in the presence of steam and catalyst. The following reactions are suggested to be included during the thermo-chemical conversion of biomass.

$$C_xH_yO_z \rightarrow (H_2 + CO_2 + CO + CH_4 + C_2 + \cdots) + \text{Tar} + \text{Char} + Q \quad (1)$$

$$C_xH_y + 2xH_2O \rightarrow xCO_2 + (2x + y/2)H_2 + Q \quad (2)$$

$$CO + H_2O \rightarrow CO_2 + H_2 - 41\ \text{kJ/mol} \quad (3)$$

$$C + H_2O \rightarrow CO + H_2 + 131.3\ \text{kJ/mol} \quad (4)$$

$$C + CO_2 \rightarrow 2CO + 162.4\ \text{kJ/mol} \quad (5)$$

$$CH_4 + H_2O \rightarrow CO + 3H_2 + 206.3\ \text{kJ/mol} \quad (6)$$

Prior to the investigations of the interactions between biomass, biochar and Ni-based catalyst, several key process parameters such as temperature have been studied. As shown in Table S2, gas yield increased from 0.34 to 0.74 g g^{-1} biomass with the increase of gasification temperature from 600 to 900 °C. From Fig. S2(a), H_2 yield increased slightly from 33.89 to 47.48 mg g^{-1} biomass when the reforming temperature increased to 900 °C. It is suggested that the decomposition of biomass (Eq. (1)) and reforming of volatiles (Eq. (2)) were intensified with increasing temperature because of the endothermic nature, resulting in the production of light gases such as H_2, CO, CO_2 and CH_4. However, char gasification (Eqs. (4) and (5)) was promoted at higher temperature resulting in more CO generation. The concentrations of other gases were reduced. Therefore, H_2 concentration was reduced from around 64–53 vol.%. In addition, water gas shift reaction (Eq. (3)) was not favored at higher temperature, and might also contribute to the reduce of hydrogen concentration at higher reaction temperature. In addition, at higher reforming temperature, the reactions of carbon gasification (Eqs. (4) and (5)) were suggested to be enhanced, promoting the further increase of CO production. In consideration of the limitations of operating costs and problematic Ni sintering for high temperature processes (Sehested et al., 2004), a proper temperature of 800 °C was suggested for the following studies about using different bio-chars as catalyst supports.

From Fig. S2(b), it can be seen that with the increase of the S/B ratio from 0 to 4, hydrogen concentration was increased from 40.54 to 50.07 vol.%, and H_2/CO increased significantly from 0.88 to 1.46 vol.%, while H_2 yield was doubled to 40.02 mg g^{-1}. It is proposed that more H_2O favored the water gas reactions and hydrocarbons reforming (Eqs. (2)–(4)) resulting in more production of H_2 and CO_2. Ni/char reactivity was also increased as more steam enhanced Eq. (4). With the further increase of the S/B ratio to 8, hydrogen yield and concentration were changed slightly. It is suggested that extra steam needed more energy to evaporate and decreased the partial reactor temperature temporarily, which weaken the reforming reactions and result in the production of large quantities of tar (Parthasarathy and Narayanan, 2014).

The effect of Ni loading on the gas distribution and yield is illustrated in Fig. S2(c). It can be found that higher loading produced a high molar fraction of H_2 and lowered content of CO_2 and CH_4. When Ni loading rising from 0 to 15 wt.%, H_2 content climbed to 50.07 vol.% and CH_4 declined to 6.61 vol.%. However, H_2 yield was decreased as loading going up to 20 wt.%. It might be due to the agglomeration at high Ni loading (Trane et al., 2012). Thus, there exists an optimum value for Ni loading (15 wt.%) was used for further studied in this work.

3.1. Interactions between the pyrolysis volatiles and the biochar/AC

In this section, the interactions between Ni, biochar and volatiles from biomass pyrolysis were studied, by carrying out experiments including three groups: (1) pyrolysis of biomass at the first stage and the derived volatiles were steam reformed at the second stage in the absence of char and activated carbon (AC) (this experiment is assigned as BIO); (2) only steam gasification of bio-chars and AC at the second stage, without biomass pyrolysis at the first stage; (3) pyrolysis of biomass at the first stage, and the pyrolysis volatiles were catalytic steam reformed at the second stage in the presence of various bio-chars and AC. The yields of hydrogen and gas are shown in Table 2.

It can be observed that for the BIO experiment (no bio-char/AC), the total gas concentration of CO, CO_2 is about 60 vol.% and the H_2 yield is very low (4.8 mg g^{-1} biomass). Regarding the second group of experiment (steam gasification with the bio-char/AC at the second stage), much higher concentrations of hydrogen and CO were obtained (a total concentration of CO and H_2 is up to 95 vol.%). Furthermore, the ratio of H_2/CO is close to 3 for the steam gasification of the bio-char/AC. Among the studied bio-chars, CC showed the highest steam gasification activity with H_2 yield of 34.62 (mg g^{-1} biomass) and gas yield of 39.45 wt.%, respectively. From Table 2,

Table 2
Biochar steam gasification properties and their effect on biomass gasification.

Catalyst	1st Group	2nd Group				3rd Group			
	BIO[a]	AC	WC	CC	RC	BIO + AC[b]	BIO + WC	BIO + CC	BIO + RC
H_2 yield, mg g^{-1} biomass	4.80	17.83	21.69	34.62	15.34	20.56	27.61	45.91	19.98
Gas yield, wt.%	34.06	37.48	13.51	39.45	17.06	66.30	52.35	81.09	45.75
Gas composition, vol.%									
H_2	18.20	48.08	74.51	61.64	63.29	35.36	46.61	50.12	42.34
CH_4	17.63	0.52	0.17	0.35	0.26	10.64	9.07	6.65	11.60
CO	35.03	21.50	21.06	24.81	20.42	20.96	26.31	21.11	22.37
CO_2	29.14	29.90	4.25	13.20	16.02	33.03	18.01	22.12	23.69

[a] Biomass pyrolysis followed by volatiles steam reforming without any char in the second stage.
[b] Biomass in the first stage and char in the second stage.

the gas yield (13–17 wt.%) and hydrogen production (14–20 mg g^{-1} biomass) from the steam gasification of WC and RC are quite low; might be attributed to that the wheat straw and rice husk have much higher ash content (~15 wt.%), as shown in Table 2. Steam gasification of the three lignocellulosic biochars in this work showed higher reactivity towards H_2 selectivity (60–75 vol.%), compared with the work carried out by Sattar et al. (2014), who reported an average H_2 content around 53 vol.% at 800 °C during steam gasification of rapeseed, wood, sewage sludge and miscanthus biochars.

Regarding the biomass gasification with bio-char (3rd group experiments), the volatiles from biomass pyrolysis were further reformed in the presence of biochar to produce more gases, resulting in the significant increase of H_2 yield as well as the concentration of syngas. Cotton char displayed the most efficient catalytic activities in terms of the reforming of pyrolysis volatiles, as the gas yield was 81.9 wt.% which is much higher than the biomass gasification without biochar (34 wt.%). Compared to the char gasification (2nd group experiments), biomass pyrolysis with char (3rd group experiments) generated much higher gas yield, although the hydrogen concentration was lower for the biomass gasification with the bio-char or AC. It is therefore suggested that the carbon conversion to gases was increased when both biomass and bio-char/AC were used. The concentration of hydrogen was reduced in each 3rd group experiment, as the fraction of H_2 was diluted by other gases such as CO_2. However, it is not clear the enhanced carbon conversion was ascribed to the biomass sample (in the 1st stage reactor) or the bio-char/CC (in the 2nd stage reactor). Therefore, the interactions between biomass and bio-char/AC were further studied.

The comparison between the calculated and experimental value of H_2 yield from biomass gasification with different bio-chars was presented in Fig. 1. The calculated value was obtained by adding up the H_2 yield from the 1st group experiment (BIO) and the 2nd group experiment (char steam gasification). The difference between the calculated value of hydrogen yield and the experimental hydrogen yield (obtained from the 3rd group experiments) was used to investigate the interactions between biochar and volatiles derived from biomass pyrolysis. As shown in Fig. 1, the experimental value of hydrogen production (45.90 mg g^{-1} biomass) was higher than the calculated value (39.42 mg g^{-1} biomass), when the cotton char was used. It is suggested that there were clear interactions between the pyrolysis volatiles and the cotton char. The WC char showed a slight positive interaction with the pyrolysis vapors, in terms of the production of hydrogen (Fig. 1). However, there was no clear difference of H_2 yield between the calculated and the experimental value of hydrogen production for the RC char. It is suggested that the highest catalytic effect of the CC was due to the presence of alkali and alkaline earth metals (AAEMs). As shown in Table S1, about 15.9 wt.% of Ca was presented inside the CC. The RC has the highest content of Si (50 wt.%, Table S1), which had almost no catalytic effect during biomass gasification (Hu et al., 2015 and Shen et al., 2015). Therefore, the poor catalytic effect of the RC was suggested due to its higher content of Si, and lower contents of AAEMs.

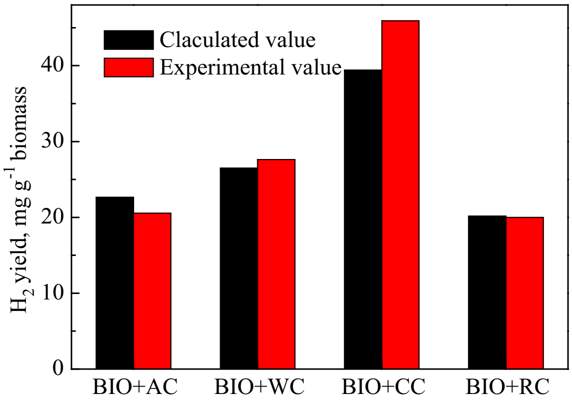

Fig. 1. Calculated and experimental value of H_2 yield using different biochar for biomass gasification.

The alkali and alkaline earth metals (AAEMs) have been reported to enhance biochar gasification activity through the increase of the absorption of H_2O molecule (Wang et al., 2015). Similar phenomenon was found by Sattar et al. (2014), who proposed that the effective catalytic role of a rapeseed biochar was mainly because of the presence of high content of K and Ca. AAEMs were also suggested to exhibit catalytic effect to the reforming of pyrolysis volatiles (Hu et al., 2015).

However, when the AC and RC were used for the gasification of biomass, there are small interactions between the pyrolysis vapor and the char. It is suggested that the production of hydrogen and carbon conversion to gas are also influenced by other factors such as the temperature distribution of the reactor, the physical contacts between materials and also the diffusion of reactants.

3.2. Investigation of the addition of Ni-based catalysts

15 wt.% of Ni was loaded on the different bio-chars and the AC. The four catalysts were used for the catalytic thermos-chemical conversion of biomass. From Fig. 2, it can be seen that a significant improvement to the gas yield was obtained with the introduction of the Ni-based catalysts. For example, an increase of H_2 yield from 27.61 to 42.48 mg g^{-1} biomass was observed when the WC catalyst was replaced by the Ni/WC. The enhancement of hydrogen production was also reported (Shen and Yoshikawa, 2014), when a Ni/char catalyst was used to compare to a biochar catalyst during biomass gasification.

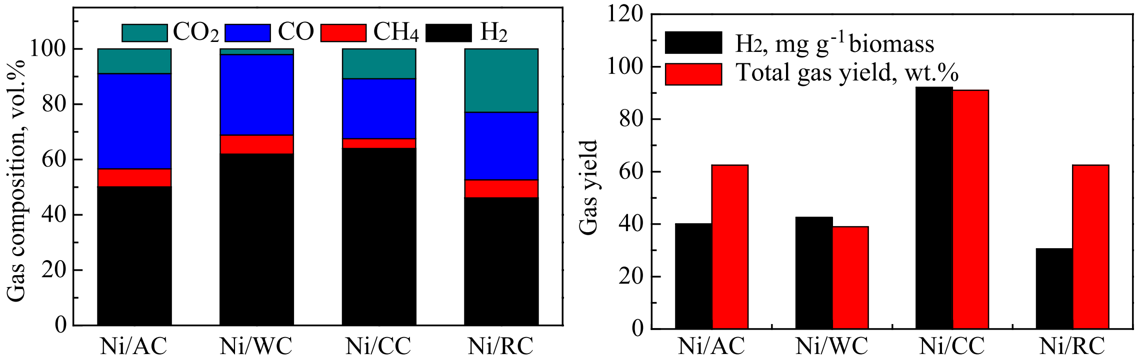

Fig. 2. Gas composition and gas yield of biomass gasification with different Ni/biochar catalyst.

The Ni/CC catalyst showed the highest catalytic activity towards H_2 production (92.08 mg g^{-1} biomass) compared to the Ni/AC, Ni/WC and Ni/RC catalysts. The highest gas yield (about 90 wt.%) was also obtained in the presence of the Ni/CC catalyst (Fig. 2). In addition, the Ni/CC and Ni/WC showed high concentration of H_2 (around 60 vol.). Therefore, the Ni-catalyst with the cotton char as support is suggested to be an efficient catalyst for hydrogen production from the thermos-chemical conversion of biomass.

As shown in Table S3, the original bio-chars showed low BET surface areas (13–28 m^2 g^{-1}), which were similar to the value reported in the literature (Zhu et al., 2015). The low surface value of pyrolysis bio-char is because of the incomplete decomposition of biomass and tar-like compounds are entrapped within the pores. However, in this work, during the preparation of Ni-based catalysts using bio-char as catalyst support, the porosity of the catalyst was increased due to the calcination step. Among the four Ni supported biochar catalysts, the Ni/CC showed the biggest surface area of 92 m^2 g^{-1} and the Ni/RC had the lowest surface area of 64 m^2 g^{-1}. The Ni/CC also had a higher external area than the other catalysts; the large external surface area of catalyst was reported to offer extra channels for the interactions between catalyst and pyrolysis volatiles (Zhu et al., 2015).

It is suggested that the presence of AAEMs is more important towards H_2 production compared to the pore structure. Zhang et al. (2016) investigated hydrogen production from biomass gasification using biochar. They reported that a demineralized biochar produced lower hydrogen yield compared with an original biochar. They also reported that a low-surface area biochar (13.21 m^2 g^{-1}) produced H_2 yield up to 65% during catalytic reforming process. In this work, the Ni/CC catalyst showed much high hydrogen production compared to the Ni/AC catalyst (Fig. 2), although the Ni/CC catalyst has much lower surface area and pore volume (Table S3). It is noted that hydrogen production (92.08 mg g^{-1} biomass) using the Ni/CC catalyst is much higher than the data reported from literatures. For example, a hydrogen yield of 50 mg g^{-1} biomass was reported by Xiao et al. (2013) using a Ni/coal-char catalyst.

Fig. S3 shows the surface morphology of the three reacted Ni/bio-char catalysts obtained from the SEM analysis. Clear visual differences of the surface morphology are observed for the three reacted catalysts, due to the nature of the bio-char and also the process of devolatilization during pyrolysis (Downie et al., 2009). Some globular particles can be easily observed on the surface of the reacted catalysts. EDX analysis for specific point was presented in Fig. S3. The globular particles mainly consist of unreacted carbon, silicon, nickel and AAEMs, which are shown in the XRF results (Table S1). In addition, the reacted Ni/CC catalyst has the lowest content of Si; this is consistent with the element analysis for the fresh chars (Table S1). Fryda et al. (2008) reported that the presence of AAEMs and Si would lead to serious agglomeration at high operation temperature. It is suggested that the globular particles were formed as a consequence of the interaction between biochar and Ni. Si presented in biochar was easily melted at high reaction temperature, resulting in the sintering of Ni together with other metals such as K, Ca and Mg. This is supported by the observations of globular particles formed on the surface of the reacted catalysts (Fig. S3). It is noted that metal sintering reduces the dispersion of catalytic active site of Ni.

4. Conclusions

The interaction between CC and volatiles contributed to the good performance of CC for H_2 production due to the presence of high content of AAEMs.

The addition of Ni metal was suggested to be more important compared to the morphologic structure in terms of hydrogen and gas production.

The Ni/CC catalyst showed much higher hydrogen production (~90 mg g^{-1} biomass) compared with the Ni/RC and the Ni/WC, might be due to the higher content of AAEMs and also the much higher external surface area.

Acknowledgements

The authors wish to express the sincere thanks to the financial support from the National Natural Science Foundation of China (51376076 and 51306066), the Special Fund for Agro-scientific Research in the Public Interest (201303095) and the Fund of State Key Laboratory of Coal Combustion (FSKLCCA1601). The experiment was also assisted by Analytical and Testing Center in Huazhong University of Science & Technology (http://atc.hust.edu.cn), Wuhan 430074 China.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.biortech.2016.05.011.

References

Chen, Y., Yang, H., Yang, Q., Hao, H., Zhu, B., Chen, H., 2014. Torrefaction of agriculture straws and its application on biomass pyrolysis poly-generation. Bioresour. Technol. 156, 70–77.

Downie, A., Crosky, A., Munroe, P., 2009. Physical Properties of Biochar. Biochar for Environmental Management Science and Technology, pp. 13–32.

Fremaux, S., Beheshti, S.-M., Ghassemi, H., Shahsavan-Markadeh, R., 2015. An experimental study on hydrogen-rich gas production via steam gasification of biomass in a research-scale fluidized bed. Energy Convers. Manage. 91, 427–432.

Fryda, L., Panopoulos, K., Kakaras, E., 2008. Agglomeration in fluidised bed gasification of biomass. Powder Technol. 181 (3), 307–320.

Hu, S., Jiang, L., Wang, Y., Su, S., Sun, L., Xu, B., He, L., Xiang, J., 2015. Effects of inherent alkali and alkaline earth metallic species on biomass pyrolysis at different temperatures. Bioresour. Technol. 192, 23–30.

Krerkkaiwan, S., Mueangta, S., Thammarat, P., Jaisat, L., Kuchonthara, P., 2015. Catalytic biomass derived tar decomposition using char from the co-pyrolysis of coal and giant leucaena wood biomass. Energy Fuels 29 (5), 3119–3126.

Liu, S., Zhu, J., Chen, M., Xin, W., Yang, Z., Kong, L., 2014. Hydrogen production via catalytic pyrolysis of biomass in a two-stage fixed bed reactor system. Int. J. Hydrogen Energy 39 (25), 13128–13135.

Liu, N., Charrua, A.B., Weng, C., Yuan, X., Ding, F., 2015. Characterization of biochars derived from agriculture wastes and their adsorptive removal of atrazine from aqueous solution: a comparative study. Bioresour. Technol. 198, 55–62.

Parthasarathy, P., Narayanan, K.S., 2014. Hydrogen production from steam gasification of biomass: influence of process parameters on hydrogen yield–a review. Renew. Energy 66, 570–579.

Sattar, A., Leeke, G.A., Hornung, A., Wood, J., 2014. Steam gasification of rapeseed, wood, sewage sludge and miscanthus biochars for the production of a hydrogen-rich syngas. Biomass Bioenergy 69, 276–286.

Sehested, J., Gelten, J.A., Remediakis, I.N., Bengaard, H., Nørskov, J.K., 2004. Sintering of nickel steam-reforming catalysts: effects of temperature and steam and hydrogen pressures. J. Catal. 223 (2), 432–443.

Sharma, A., Pareek, V., Zhang, D., 2015. Biomass pyrolysis—a review of modelling, process parameters and catalytic studies. Renew. Sustain. Energy Rev. 50, 1081–1096.

Shen, Y., 2015. Chars as carbonaceous adsorbents/catalysts for tar elimination during biomass pyrolysis or gasification. Renew. Sustain. Energy Rev. 43, 281–295.

Shen, Y., Yoshikawa, K., 2014. Tar conversion and vapor upgrading via in situ catalysis using silica-based nickel nanoparticles embedded in rice husk char for biomass pyrolysis/gasification. Ind. Eng. Chem. Res. 53 (27), 10929–10942.

Shen, Y., Zhao, P., Shao, Q., Takahashi, F., Yoshikawa, K., 2015. In situ catalytic conversion of tar using rice husk char/ash supported nickel–iron catalysts for biomass pyrolytic gasification combined with the mixing-simulation in fluidized-bed gasifier. Appl. Energy 160, 808–819.

Song, Y., Wang, Y., Hu, X., Hu, S., Xiang, J., Zhang, L., Zhang, S., Min, Z., Li, C.-Z., 2014. Effects of volatile–char interactions on in situ destruction of nascent tar during the pyrolysis and gasification of biomass. Part I. Roles of nascent char. Fuel 122, 60–66.

Srinakruang, J., Sato, K., Vitidsant, T., Fujimoto, K., 2005. A highly efficient catalyst for tar gasification with steam. Catal. Commun. 6 (6), 437–440.

Tang, Q., Bian, H., Ran, J., Zhu, Y., Yu, J., Zhu, W., 2015. Hydrogen-rich gas production from steam gasification of biomass using CaO and a Fe–Cr water–gas shift catalyst. BioResources 10 (2), 2560–2569.

Trane, R., Dahl, S., Skjøth-Rasmussen, M.S., Jensen, A.D., 2012. Catalytic steam reforming of bio-oil. Int. J. Hydrogen Energy 37 (8), 6447–6472.

Wang, D., 2013. Study of Ni/char catalyst for biomass gasification in an updraft gasifier: influence of catalyst granular size on catalytic performance. BioResources 8 (3), 3479–3489.

Wang, D., Yuan, W., Ji, W., 2011. Char and char-supported nickel catalysts for secondary syngas cleanup and conditioning. Appl. Energy 88 (5), 1656–1663.

Wang, S., Zhang, F., Cai, Q., Zhu, L., Luo, Z., 2015. Steam reforming of acetic acid over coal ash supported Fe and Ni catalysts. Int. J. Hydrogen Energy 40 (35), 11406–11413.

Weerachanchai, P., Horio, M., Tangsathitkulchai, C., 2009. Effects of gasifying conditions and bed materials on fluidized bed steam gasification of wood biomass. Bioresour. Technol. 100 (3), 1419–1427.

Wu, C., Williams, P.T., 2009. Hydrogen production by steam gasification of polypropylene with various nickel catalysts. Appl. Catal. B 87 (3–4), 152–161.

Wu, C., Williams, P.T., 2011. Nickel-based catalysts for tar reduction in biomass gasification. Biofuels 2 (4), 451–464.

Xiao, X., Cao, J., Meng, X., Le, D.D., Li, L., Ogawa, Y., Sato, K., Takarada, T., 2013. Synthesis gas production from catalytic gasification of waste biomass using nickel-loaded brown coal char. Fuel 103, 135–140.

Yan, F., Luo, S.-Y., Hu, Z.-Q., Xiao, B., Cheng, G., 2010. Hydrogen-rich gas production by steam gasification of char from biomass fast pyrolysis in a fixed-bed reactor: influence of temperature and steam on hydrogen yield and syngas composition. Bioresour. Technol. 101 (14), 5633–5637.

Yang, H., Liu, B., Chen, Y., Chen, W., Yang, Q., Chen, H., 2016. Application of biomass pyrolytic polygeneration technology using retort reactors. Bioresour. Technol. 200, 64–71.

Yao, D., Wu, C., Yang, H., Hu, Q., Nahil, M.A., Chen, H., Williams, P.T., 2014. Hydrogen production from catalytic reforming of the aqueous fraction of pyrolysis bio-oil with modified Ni–Al catalysts. Int. J. Hydrogen Energy 39 (27), 14642–14652.

Zhang, S., Chen, Z., Cai, Q., Ding, D., 2016. The integrated process for hydrogen production from biomass: Study on the catalytic conversion behavior of pyrolytic vapor in gas–solid simultaneous gasification process. Int. J. Hydrogen Energy 41 (16), 6653–6661.

Zhao, Z., Lakshminarayanan, N., Swartz, S.L., Arkenberg, G.B., Felix, L.G., Slimane, R.B., Choi, C.C., Ozkan, U.S., 2015. Characterization of olivine-supported nickel silicate as potential catalysts for tar removal from biomass gasification. Appl. Catal. A 489, 42–50.

Zhu, L., Yin, S., Yin, Q., Wang, H., Wang, S., 2015. Biochar: a new promising catalyst support using methanation as a probe reaction. Energy Sci. Eng. 3 (2), 126–134.