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# Hydrogen production via steam reforming of acetic acid over biochar-supported nickel catalysts

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## ABSTRACT

Development of high-performance and low-cost catalysts will make the biomass-derived hydrogen production technology, steam reforming of bio-oil, becomes to be more and more economical and promising. Biochar, which was produced via fast pyrolysis of rice husk, was activated by different methods, and then it was used as a support for the nickel catalyst, and tested in the steam reforming of acetic acid. The physicochemical properties of the Ni/biochar (BCx) catalysts were characterized by BET, XRD, SEM, TEM and H<sub>2</sub>-TPR. The development of pore structure and improvement of surface properties were achieved by the activation. Subsequently, the activity of several catalysts on hydrogen production was investigated. It was found that the Ni/BC4 catalyst (biochar activated by KOH alkalinization coupled with HNO<sub>3</sub> reflux) exhibited the best catalytic performance. Under the conditions of T = 700 °C, S/C = 2.5 and LHSV = 10 h<sup>-1</sup>, the carbon conversion and hydrogen yield reached to 91.2% and 71.2%, respectively.

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## Introduction

The bio-oil produced via biomass fast pyrolysis is supposed to be a substitute for fossil fuels [1,2]. However, the inferior properties of crude bio-oil, including high oxygen and moisture contents, poor thermal stability and strong corrosiveness [3], have severely limited the direct utilization of bio-oil. The crude bio-oil could be upgraded by catalytic hydrogenation [4,5] and cracking [6,7] to produce high-quality liquid fuels. However, direct cracking of bio-oil usually results in serious coke deposition and rapid catalyst deactivation due to the low H/C<sub>eff</sub> ratio [8]. As the H/C<sub>eff</sub> ratio increases, the reaction activity is notably enhanced and the coke deposition is significantly suppressed [9]. Therefore, in order to increase the H/C<sub>eff</sub> ratio of bio-oil to improve the upgrading process, a large number of hydrogen is desired. The hydrogen could be

efficiently produced by the steam reforming of water-rich fraction or some compounds (acids and ketones, etc.) from bio-oil [10,11]. Various catalysts have been investigated to achieve the efficient hydrogen production and conversion of bio-oil, comprising different active metals (Ni, Pd, Rh, Co, Mg, etc.) [10,12–15] and supports (Al<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, SBA-15, etc.) [16–18]. Among these catalysts, Ni-based catalysts (such as Ni/Al<sub>2</sub>O<sub>3</sub>, Ni/SiO<sub>2</sub>, Ni/ZrO<sub>2</sub>, etc.) are widely used and have attracted extensive attentions due to the high activity and relatively low cost [19–21]. And the conventional Ni-based catalyst could also be modified by various methods for efficient hydrogen production [22–24].

Biochar, a solid byproduct generated by biomass fast pyrolysis, accounts for 15–25 wt% of the biomass feedstock [25], and thus the development of biochar is of great significance to achieve the high-value utilization of pyrolytic products.

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Nowadays, biochar is mainly used for soil fertility improvement [26], carbon sequestration [27], soil remediation [28], wastewater treatment [29–31] and other fields [32–34]. Biochar-based catalysts have attracted extensive attentions due to the low cost and porous property. Mani et al. [35] carried out the catalytic decomposition of toluene catalyzed by pine bark biochar and found that the toluene conversion rose from 13% to 94% as the temperature increased from 600 °C to 900 °C. In order to improve the properties of biochar, different treatment methods have been used including chemical and physical activation to obtain activated biochar (ABC). Muradov et al. [36] prepared the biochar activated by CO<sub>2</sub> and H<sub>2</sub>O under high temperatures for the steam reforming of biogas. The ABC exhibited a much better catalytic performance than the original biochar. Dehkhoda et al. [37] used biochar as a solid acid catalyst for biodiesel production. The result showed that the surface area of biochar pretreated by KOH and H<sub>2</sub>SO<sub>4</sub> was significantly increased, and the enhanced surface area and acid density led to a better reaction activity. Wang et al. [38] performed the methanation of bio-syngas over Ru/ABC catalysts and revealed that the larger surface area of ABC could ensure the high dispersion of Ru particles on the catalyst support. The CO conversion and selectivity of CH<sub>4</sub> reached 97% and 92%, respectively. It was also reported by Zhu et al. [39] that Ru/ABC catalyst showed superior catalytic performance compared to the conventional activated carbon supported Ru catalyst in the methanation of bio-syngas.

In this study, biochar was tested for the possible using of catalyst support in the steam reforming of bio-oil. Firstly, the biochar was activated via different methods to enlarge its specific surface and promote its porosity. Then it was used as a support to load the Ni metal to form Ni/biochar catalyst. Finally, the steam reforming of acetic acid for hydrogen production was carried out to test the performance of Ni/biochar catalyst.

## Experimental section

### Catalyst preparation

The biochar was produced by fast pyrolysis of rice husk at 500 °C in a fluidized bed reactor and was further activated by following methods:

**Heat activation:** Biochar was heated at 700 °C for 2 h in a tube furnace under an atmosphere of N<sub>2</sub>. The activated sample was denoted as BC1.

**KOH alkalinization:** Biochar was impregnated in an aqueous solution of KOH (5 mol/L) for 4 h at ambient temperature, and then filtered and dried for 36 h at 110 °C. Afterwards, the sample was calcined at 700 °C for 2 h in a tube furnace under an atmosphere of N<sub>2</sub>. Finally, the sample was washed with deionized water until neutral and dried at 110 °C overnight. The final sample was denoted as BC2.

**HNO<sub>3</sub> acidification:** The procedure was the same as “KOH alkalinization” except for “Biochar was impregnated in an aqueous solution of HNO<sub>3</sub>” in the first step. The final sample was denoted as BC3.

**KOH alkalinization coupled with HNO<sub>3</sub> acidification:** The BC2 was refluxed in the 30% aqueous solution of HNO<sub>3</sub> for 6 h at

100 °C. Then, the sample was filtered, washed, and dried as described above. The final sample was denoted as BC4.

The preparation procedure of biochar-based catalysts was as follows: a certain amount of BC1, BC2, BC3, BC4 and BC5 (the original biochar) were added into the aqueous solution of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.085 mol/L), respectively. The suspension was stirred for 6 h at ambient temperature, and then filtered and dried overnight at 110 °C. The samples were calcined at 500 °C for 2 h in a tube furnace under an atmosphere of N<sub>2</sub> to obtain the Ni/BC1, Ni/BC2, Ni/BC3, Ni/BC4 and Ni/BC5 catalysts. The loading amounts of Ni for all the catalysts were 10 wt%.

### Catalyst characterization

The Brunauer-Emmett-Teller (BET) surface areas ( $S_{\text{BET}}$ ) of the catalysts were measured by N<sub>2</sub> physical adsorption. N<sub>2</sub> adsorption-desorption isotherms were recorded at –196 °C using a Tristar II 3020 apparatus (Micromeritics). Before the test, the sample was degassed at 300 °C for 3 h. The surface area was obtained by Brunauer-Emmett-Teller (BET) method, and the pore size and volume were calculated according to the Barrett-Joyner-Halenda (BJH) model. Powder X-ray diffraction (XRD) patterns were characterized on a PANalytical X'Pert PRO X-ray diffractometer with a Cu-K<sub>α</sub> radiation source at 40 kV and 30 mA. The diffraction angle  $2\theta$  ranged from 10° to 90°. The surface morphologies were observed by scanning electron microscopy (SEM) using FEI SIRION-100 apparatus. The active metals and their distribution were observed by transmission electron microscopy (TEM) using Philips-FEI Tecnai G2F30 apparatus. The particle sizes were calculated as follows:  $d = \sum n_i d_i^3 / \sum n_i d_i^2$ , where  $d_i$  was the specific particle size and  $n_i$  was the corresponding particle number [40]. Hydrogen temperature programmed reduction (H<sub>2</sub>-TPR) was conducted on a Micromeritics AutoChem II 2920 instrument. The samples were purged by argon at 200 °C for 1.5 h and then cooled to

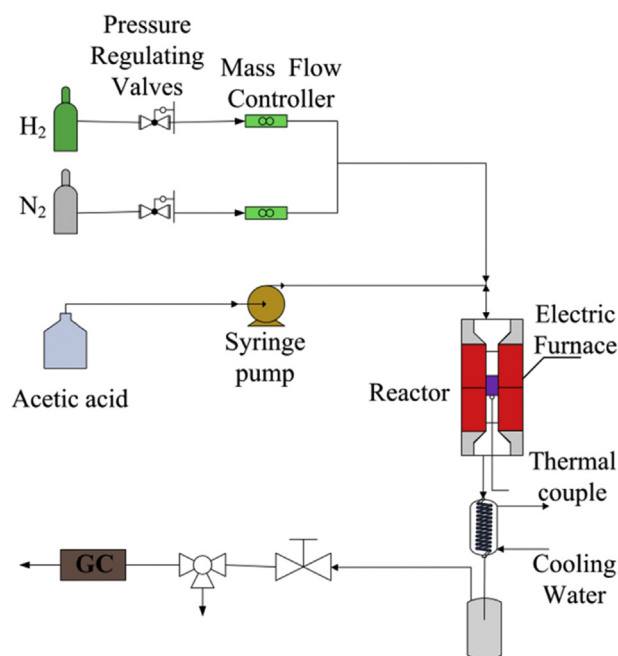


Fig. 1 – The experimental reactor for steam reforming.

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