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# Catalytic steam reforming of bio-oil model compounds for hydrogen-rich gas production using bio-char as catalyst

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## ABSTRACT

Hydrogen-rich gas production from the catalytic steam reforming of bio-oil model compounds was carried out in a fixed bed reactor. Bio-char, which was obtained from biomass gasification process and contained many alkali and alkaline metallic (AAEM) species, was used as a catalyst. The results showed that bio-char was effective in enhancing catalytic steam reforming of bio-oil model compounds and producing hydrogen rich gas. Temperature, S/B and WHSV were the operating variables which affected to a great extent of hydrogen production. The yield and concentration of hydrogen reached high values of 89.13% and 75.97%, respectively, under the condition of 900 °C, S/B of 3 and WHSV = 1. Acid treatment of bio-char was conducted to investigate the effect of inherent AAEM species on the catalytic activity of bio-char. It was found that the inherent AAEM species appear to have significant effect on the catalytic activity of bio-char especially the water-gas shift reaction under the current experimental conditions.

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## Introduction

Hydrogen has many advantages due to its high combustion efficiency, nonpolluting and light weight, which make it able to be considered as an ideal energy medium and alternative to fossil fuels such as oil and coal [1,2]. Biomass is one of the most abundant renewable resources available for hydrogen production by thermo-chemical processes or biological processes. In recent years, various technologies have been developed about the steam reforming of bio-oil for hydrogen production [3–5]. A major advantage for this process is that bio-oil is much easier and less expensive to transport than either biomass or hydrogen [6,7].

However, bio-oil is a mixture of hundreds of components, such as carboxylic acids, aldehydes, ketones, alcohols and phenols, which was significant influenced by the type of biomass and reaction conditions [8,9]. Thus, model compounds are often used to research the catalytic activity of reforming catalyst. One of the great challenges in the developing bio-oil reforming process is to reduce the content of tar which often causes the coking, blockage or other problems. A variety of catalysts such as minerals [10,11], Ni-based catalysts [12,13] and Iron-based catalysts [14,15] have been studied in tar reforming. These catalysts have the high activity to reform tar, but they are expensive and can be easily deactivated or poisoned in the reforming process. Some previous studies [16–20] have clearly indicated that char or ash from biomass

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and coal have high activity for bio-oil reforming. However, char is an effective catalyst for light components removal but lacks sufficient reactivity for heavy components [20,21]. The coke deposited on the surface of char can block the pores and reduce the surface area, thus it lead to decrease the activity of char. However, the deposited coke can be converted by gasification or reforming agents, such as steam, O<sub>2</sub> and CO<sub>2</sub>, which would inhibit its deactivation through producing new pores [18,22]. If deactivated, these catalysts can be simply burned or gasified to recover their energy without the need of regeneration [23].

Biomass may contain a significant amount of inherent alkali and alkaline metallic (AAEM) species as a result of nutrients uptake during growth [24]. After biomass gasification, most of the inherent AAEM species may be retained in the char. It is well-known that alkali (K, Na) and alkaline earth metals (Mg, Ca) can significantly promote the catalytic activity of bio-char for bio-oil reforming by increasing the water adsorption on the surface [25,26]. Kongvui Yip [27] studied the effect of alkali and alkaline metallic (AAEM) species on bio-char reactivity and syngas compositions during steam gasification. The results indicated that Na, K and Ca retained in the bio-chars are the key catalytic species, with the catalytic effect appearing to be in the order K > Na > Ca during the steam gasification reaction of these bio-chars. Daniel Mourant [28] studied the effects of alkali and alkaline earth metallic species on the yield and composition of bio-oil. The results indicated that the removal of AAEM species did not result in significant changes in the yields of bio-oil and bio-char. However, the bio-oil properties, e.g. viscosity, were drastically affected by the removal of AAEM species. Furthermore, with the utilization of low cost bio-char, the economics of hydrogen production from bio-oil catalytic reforming can be improved dramatically. Another advantage of using bio-char based catalysts for bio-oil reforming is that carbon-based catalysts are quite resistant to deactivation by sulfur-containing bio-oil. Therefore, bio-char have great potential to be the catalyst in bio-oil reforming process.

In this paper, bio-char, as a by-product of the biomass gasification process, was used as catalyst in the catalytic steam reforming of bio-oil model compounds for hydrogen rich gas production in a fixed bed reactor. Our objective is to study the catalytic behavior of bio-char and the effect of inherent AAEM species on the catalytic activity of bio-char.

## Experimental and methods

### Bio-oil model compounds

The bio-oil model compounds were obtained by the blend of acetic acid (CH<sub>3</sub>COOH), m-cresol (C<sub>7</sub>H<sub>8</sub>O), furfural (C<sub>5</sub>H<sub>4</sub>O<sub>2</sub>) and acetone (CH<sub>3</sub>COCH<sub>3</sub>). All reagents were analytical grade and provided by Sinopharm Chemical Reagent Co. Ltd. (Beijing, China).

### Bio-char preparation

Bio-char used in this study was obtained as the by-product of biomass gasification process. The ultimate and proximate analysis of the bio-char were reported in Table 1.

**Table 1 – Ultimate analysis and proximate analysis of the bio-char.<sup>a</sup>**

Ultimate analysis (wt.%)				Proximate analysis (wt.%)		
C	H	O <sup>b</sup>	N	Volatile matter	Fixed carbon	Ash
60.10	3.68	4.49	0.13	30.90	37.50	31.60

<sup>a</sup> Dry basis.  
<sup>b</sup> By difference.

AAEM species were removed by submitting the bio-char to washing with dilute hydrochloric acid (10 wt.%) for 5 h at room temperature. The bio-char sample was then rinsed with deionized water until neutrality was achieved. All samples were filtered with a 30 μm stainless steel mesh to separate the bio-char from the leaching water before being dried and weighed.

The alkali and alkaline earth metallic (AAEM) species in bio-char were quantified using X-ray fluorescence spectrometer (XRF-1800). The result of AAEM species analysis were reported in Table 2.

### Apparatus and procedures

A schematic flow sheet was shown in Fig. 1. The apparatus include syringe pump, fixed bed reactor, thermocouple, temperature controller, mass flow controller, cooler, dryer and gas analyzer. The fixed bed reactor was made up of stainless steel with a length 60 cm and an inner diameter 25 mm. A porous distributor was installed at 30 cm from the bottom of the reactor to support the bed material. The heat was provided by an electric furnace and the reaction temperature was monitored and controlled by a thermocouple. The liquid feedstock was fed into the reactor by using a syringe pump. The experimental temperature was controlled between 750 °C and 900 °C in 50 °C steps, S/B (steam to bio-oil model compounds ratio) was varied from 1 to 7 and WHSV (weight hourly space velocity) was between 1 and 4. The quartz was used in the comparison experiment with no catalyst.

In this study, before each experiment the bio-char was treated with steam to remove the volatile matter and fixed carbon for 1 h at 900 °C. The ultimate analysis of the bio-char after steam pretreatment are reported in Table 3. The BET results were measured by Brunauer Emmett Teller (BET) method (ASAP 2000), and shown in Table 4.

### Product analysis

Non-condensable gases composed of H<sub>2</sub>, CO, CO<sub>2</sub> and CH<sub>4</sub> were analyzed by infrared gas analyser (Gasboard-3100).

**Table 2 – AAEM species analysis of the ash in bio-char (wt. %).**

Sample	Mg	Ca	K	Fe	Al	Zn
Raw bio-char	17.16	13.18	2.10	2.16	1.71	0.22
Acid-treated bio-char	5.19	3.36	1.16	0.93	1.15	0.06

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