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Hydrogen Production From Crude Bio-oil and Biomass Char by Electrochemical Catalytic Reforming

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We reports an efficient approach for production of hydrogen from crude bio-oil and biomass char in the dual fixed-bed system by using the electrochemical catalytic reforming method. The maximal absolute hydrogen yield reached 110.9 g H_2/kg dry biomass. The product gas was a mixed gas containing 72%H_2, 26%CO_2, 1.9%CO, and a trace amount of CH_4. It was observed that adding biomass char (a by-product of pyrolysis of biomass) could remarkably increase the absolute H_2 yield (about 20%−50%). The higher reforming temperature could enhance the steam reforming reaction of organic compounds in crude bio-oil and the reaction of CO and H_2O. In addition, the CuZn-Al_2O_3 catalyst in the water-gas shift bed could also increase the absolute H_2 yield via shifting CO to CO_2.

Key words: Hydrogen, Bio-oil, Biomass char, Ni-Al_2O_3 catalyst, CuZn-Al_2O_3 catalyst, Electro chemical catalytic reforming

I. INTRODUCTION

Hydrogen is recognized as a clean fuel and energy carrier and will play an important role in the future global economy. In particular, its production is an attractive subject of current interest for fuel cell applications [1, 2], which are considered to have the potential to provide a clean energy source for automobile as an alternative to gasoline or diesel engines. Hydrogen is also one of most important chemicals and is widely used for ammonia production, oil refineries, and methanol production etc. Currently, main processes for producing commercial hydrogen are catalytic steam reforming of natural gas and oil-derived naphtha, partial oxidation of heavy oils, gasification of coal as well as electrolysis of water [3, 4]. In view of growing environmental concerns such as global warming and the depletion of fossil fuel, major efforts are being dedicated to develop the utilization of renewable energy sources. Real environmental benefits will be linked to the ability to produce hydrogen from renewable sources with no net production of greenhouse gas such as CO_2 [5]. Biomass has been proposed as an alternative to produce hydrogen, because this renewable rich resource does not contribute to a net increase in atmospheric CO_2 [6].

There are different routes proposed for biomass conversion into hydrogen or hydrogen-rich gas, mainly including thermochemical conversion and bio-chemical/biological conversion [7, 8]. For production of hydrogen by thermochemical conversion such as biomass gasification [9, 10], biomass catalytic pyrolysis [11, 12], and catalytic steam reforming of liquids derived from biomass (bio-oil) *etc.* [13, 14] have been widely investigated. Gasification is the conversion of biomass into a combustible gas mixture (*e.g.*, H_2, CO, CH_4 *etc.*) by the partial oxidation of biomass at high temperatures (typically in 800−900 °C) [15]. The route of the catalytic steam reforming of bio-oil and biomass char for hydrogen production involves fast pyrolysis of biomass to generate bio-oil and biomass char, reforming of bio-oil and biomass char to produce a gaseous rich-hydrogen mixture.

Bio-oil is dark-brown organic liquid and contains a large number of complex compounds such as acids, alcohols, aldehydes, ketones, substituted phenolics, and other oxygenates derived from biomass carbohydrates and lignin [16]. The distribution of these compounds depends on the type of biomass used and the pyrolysis process conditions (carrier gas, temperature, residence time, and heating rate, *etc.*) [17]. The oxygenated organic compounds in the bio-oil can be simply described as a chemical formula of $C_nH_mO_k$, and the steam reforming of the bio-oil proceeds according to the following stoichiometric reactions [18]:
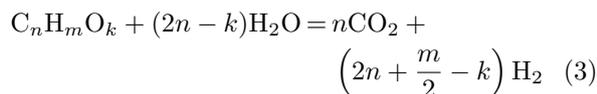
$$C_nH_mO_k + (n-k)H_2O = nCO + \left(n + \frac{m}{2} - k\right)H_2 \quad (1)$$
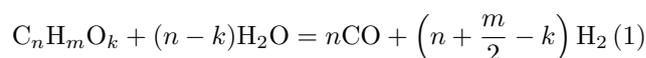
and the following water-gas shift (WGS):

$$CO + H_2O = CO_2 + H_2 \quad (2)$$
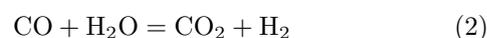
Thus, the overall steam reforming reaction can be given

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by

$$C_nH_mO_k + (2n-k)H_2O = nCO_2 +$$
$$\left(2n + \frac{m}{2} - k\right)H_2 \quad (3)$$

In our previous work, much attention has been paid to the fast pyrolysis of biomass [19−21], the production of hydrogen or bio-syngas from the volatile fraction of the bio-oil and its model compounds [22−27], and the synthesis of liquid bio-fuels such as gasoline and diesel *etc.* [24]. A novel electrochemical catalytic reforming (ECR) method for efficient production of hydrogen from the volatile fraction of the bio-oil and its compounds was developed in our lab [25−27]. In this work, we efficiently produce hydrogen from the crude bio-oil and biomass char in the pyrolysis proportion of biomass over commercial catalyst. An efficient and promising reforming approach for producing hydrogen from crude bio-oil and biomass char was proposed and investigated. The commercial reforming catalyst Ni-Al$_2$O$_3$ (Ni: 16%, 40−60 mesh) was used in ECR process and the commercial water-gas shift catalyst CuZn-Al$_2$O$_3$ (CuO: 60%, ZnO: 30%, Al$_2$O$_3$: 10%, 40−60 mesh) was used in WGS process.

II. EXPERIMENTS

A. Feedstock

The crude bio-oil and biomass char used in this work was produced by the fast pyrolysis of biomass in a circulating fluidized bed with a capacity of 120 kg/h of oil at our Lab (Anhui Province Key Laboratory of the Biomass Clean Energy, Hefei, China). The pyrolysis temperature of the biomass (*i.e.*, corn stalk) was about 505 °C. Some properties of the crude bio-oil and biomass char are given in Table I. The moisture content of crude bio-oil was 24.4%. The density of crude bio-oil was 1.16 Mg/m^3. The lower heating value (LHV) of crude bio-oil was 17.77 MJ/kg. The pH of crude bio-oil was 3.3. The oxygenated organic compounds in crude bio-oil can be represented as an overall chemical formula of CH$_{1.47}$O$_{0.49}$·0.38H$_2$O.

B. Reaction system for hydrogen production

As shown in Fig.1, the reaction for producing hydrogen from crude bio-oil and biomass char was carried out in a dual fixed-bed system with a reforming bed and a water-gas shift bed under atmospheric pressure. The whole dual fixed-bed system was a quartz tube reactor containing two fixed-beds. The upper one was named as "reforming bed" and filled with the mixture of 12 g Ni-Al$_2$O$_3$ (40−60 mesh) catalyst and 2.2 g biomass char (biomass char: <100 mesh). It was used to reform
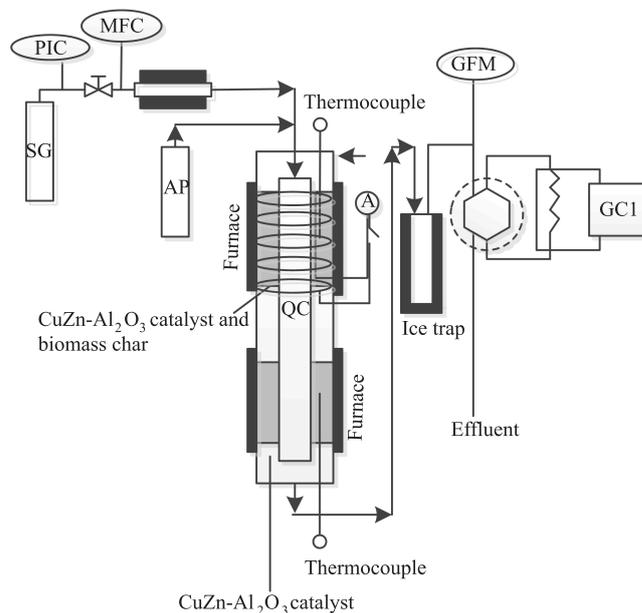
FIG. 1 Schematic diagram of the reforming/water-gas shift dual fixed-beds reaction system for production of hydrogen from crude bio-oil and biomass char. SG=steam generator, BP=bio-oil pump, PIC=pressure indicator controller, MFC=mass flow controller, QC=quarts column, GFM=gas flow meter, and GC=gas chromatogram.

TABLE I The elemental compositions of crude bio-oil and biomass char derived from corn stalk through fast pyrolysis technology.

Elements	C/%	H/%	N/%	Other[a]
Crude bio-oil	42.3	7.9	0.3	49.5
Biomass char	65.16	2.935	0.33	31.575

[a] O, S, and ash *etc.*

crude bio-oil. The other fixed-bed (named as "water-gas shift bed"), which was filled with 9 g CnZn-Al$_2$O$_3$ (40−60 mesh) catalyst, was used for CO to CO$_2$ shifting.

An annular Ni-Cr wire (resistance: 15 Ω) used for heating the catalyst and providing the thermal electrons onto the catalyst was enwound on a small quartz column. Then it was installed in the reforming bed. The mixture was uniformly embedded around the Ni-Cr wire, through which a given electric current passed. The CuZn-Al$_2$O$_3$ catalyst was filled in the water-gas shift bed. To create certain reforming temperature (T) and water-gas shift temperature (T_s), the reforming bed and the water-gas shift bed were heated by an outside furnace respectively. What must be mentioned is that T_s of the water-gas shift bed was hold at 220 °C [28].

The operation procedures of the system were arranged as follows: firstly, the quartz tube reactor was flushed out by flowing pure N$_2$. Both the reforming bed and water-gas shift bed were respectively heated to the

given temperatures. Then the crude bio-oil was continuously fed into the reactor at the rate of 16.5 g/h using a micro-injection pump (model: TS2-60, Baoding Longer Precision Pump). The steam from a steam generator was preheated and fed into the reactor for adjusting the S/C ratio (molar ratio of steam to carbon).

In order to research the performances of hydrogen production from different routes, the experiments were carried out as following: (i) the steam reforming reactions of crude bio-oil with and without biomass char; (ii) the reactions for production hydrogen using the crude bio-oil and biomass char at different reforming temperatures and currents; (iii) using downstream CuZn-Al$_2$O$_3$ catalyst to decrease CO content in the product gases.

C. Experimental measurements and definitions

The final gaseous products of H$_2$, CO, CO$_2$, and CH$_4$ were measured by gas chromatograph GC (Model: SP-6800A, TDX-01) with thermal conductivity detector (TCD), using ultra-high purity argon (99.999%) as carrier gas. The performance of crude bio-oil and the biomass char catalytic steam reaction was studied by measuring the absolute H$_2$ yield, the carbon conversion of crude bio-oil to gases ([C]$_{conv}$), and the distribution of product gases from the reaction for production hydrogen using crude bio-oil and biomass char. It is well known that the bio-oil and biomass char are the production of the fast pyrolysis of biomass. In order to obtain the maximal hydrogen quality, the absolute H$_2$ yield was researched which is defined as the hydrogen quality (g) produced by the crude bio-oil and biomass char from 1 kg dry biomass. The carbon conversion is calculated according to Eq.(4) and expressed as the percentage of carbon from fed crude bio-oil to the final gaseous products (*i.e.*, CO, CO$_2$, and CH$_4$).

$$[C]_{conv} = \frac{x_{C,gas}}{x_{C,feed}} \times 100\% \tag{4}$$

which $x_{C,gas}$ and $x_{C,feed}$ are moles of carbons in the gaseous and in the feed, respectively.

III. RESULTS AND DISCUSSION

A. Influence of biomass char

In order to make a contrast, the steam reforming reactions of crude bio-oil with and without biomass char were both carried out in the dual fixed-bed system. The reforming conditions were T=500−800 °C, I=0 A, P=101 kPa, f(bio-oil fed rate)=16.5 g/h, S/C= 11, GHSV=6200 h^{-1}. Figure 2 shows the function of biomass char on the absolute H$_2$ yield (a) and the carbon conversion (b). At the same reforming temperature, the absolute H$_2$ yield and carbon conversion were increased by adding biomass char. At 800 °C,
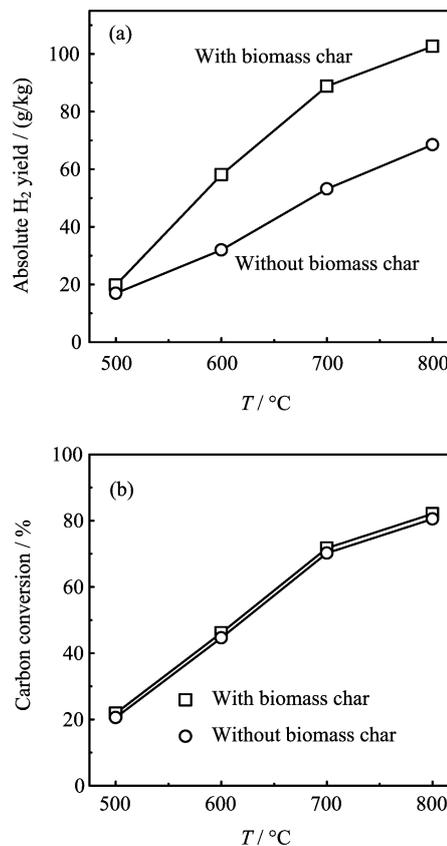

FIG. 2 Effect of biomass char on (a) absolute H$_2$ yield and (b) carbon conversion of bio-oil fed. Conditions: T=500−800 °C, P=101 kPa, f=16.5 g/h, Ni-Al$_2$O$_3$ catalyst/biomass char=12 g/2.2 g, S/C=11, GHSV=6200 h^{-1}.

the absolute H$_2$ yield was 102.6 g H$_2$/kg dry biomass and the carbon conversion was 82% with biomass char. However, the absolute H$_2$ yield was only 68.5 g H$_2$/kg dry biomass and the carbon conversion was only 80.5% without biomass char at the same reforming temperature. As shown in Fig.3, At 800 °C, without biomass char the H$_2$ content were 72.3%. But with biomass char the H$_2$ content decreased to 71.2%. It is because that adding biomass char would change the volume ratio of H$_2$ to CO$_2$ in the product gases. The reactions of crude bio-oil and biomass char could be summarized as follows:

$$CH_{1.47}O_{0.49} + 1.51H_2O = 2.245H_2 + CO_2 \tag{5}$$
$$C + 2H_2O = 2H_2 + CO_2 \tag{6}$$
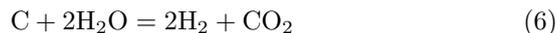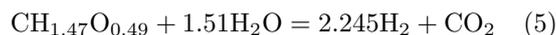
without biomass char, the volume ratio of H$_2$ to CO$_2$ should be 2.245:1 (Eq.(5)). But after adding biomass char (Eq.(6)), the volume ratio of H$_2$ to CO$_2$ would be reduced due to the increased CO$_2$ content. But the absolute H$_2$ yield was increased because of the contribution of biomass char (Eq.(6)). The increased carbon conversion could be comprehended like this: adding biomass char would make part of the product carbon
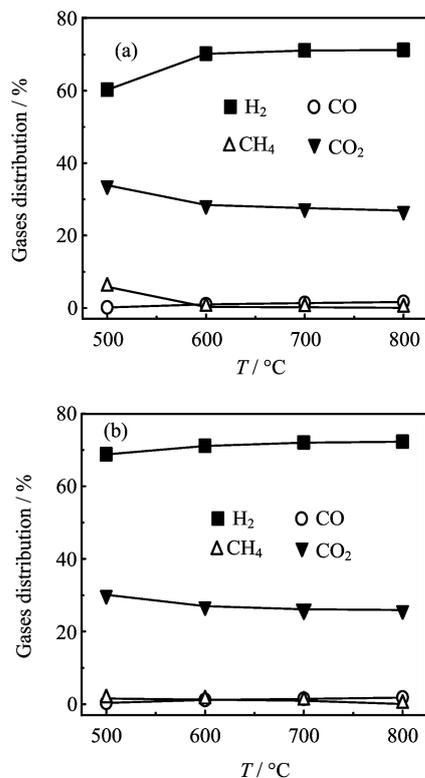
FIG. 3 Effect of biomass char on distribution of main product gases. (a) With biomass char and (b) without biomass char. Conditions: $T=500-800$ °C, $P=101$ kPa, $f=16.5$ g/h, Ni-Al$_2$O$_3$ catalyst/biomass char=12 g/2.2 g, S/C=11, GHSV=6200 h^{-1}.
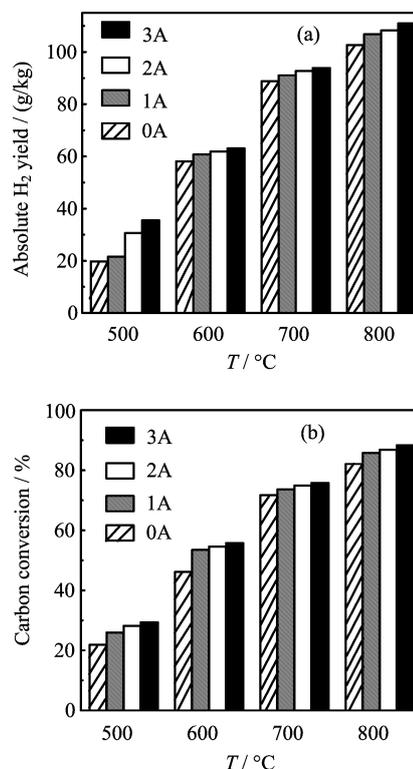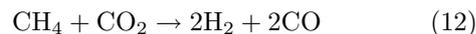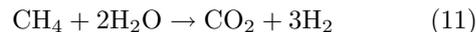

FIG. 4 Effect of the current on (a) absolute H$_2$ yield and (b) carbon conversion in the reaction for producing hydrogen using crude bio-oil and biomass char. Conditions: $T=500-800$ °C, $I=0-3$ A, $P=1$ kPa, $f=16.5$ g/h, Ni-Al$_2$O$_3$ catalyst/biomass char=12 g/2.2 g, S/C=11, GHSV=6200 h^{-1}.

from crude bio-oil deposit on the biomass char instead of on the Ni-Al$_2$O$_3$ catalyst.

B. Influence of reforming temperature

The influence of the reforming temperature on absolute H$_2$ yield, carbon conversion and distribution of main product gases was investigated in the reaction for producing hydrogen using crude bio-oil and biomass char. The absolute H$_2$ yield and carbon conversion remarkably increased with the increasing reforming temperature. The absolute H$_2$ yield increased from 19.7 g H$_2$/kg dry biomass to 102.6 g H$_2$/kg dry biomass and the carbon conversion increased from 21.8% to 82% when the reforming temperature increased from 500 °C to 800 °C. Figure 3(a) shows the influence of reforming temperature on distribution of main product gases. The H$_2$ and CO content increased with the increasing reforming temperature, indicating that the thermal decomposition of the oxygenated organic compounds increased at the higher temperature. On the other hand, the CH$_4$ and CO$_2$ content appeared an opposite trend. The H$_2$ and CO contents increased from 60.2% and 0.15% to 71.2% and 1.67%, respectively, but the

CH$_4$ and CO$_2$ contents reduced from 5.82% and 33.9% to 0.05% and 26.8% as the reforming temperature increased from 500 °C to 800 °C. The above phenomena could be understood as follows: the reforming reaction is an endothermic reaction, and the increasing reforming temperature would increase the reforming reaction rate. The reforming reaction would be in favor of higher reforming temperature region. The detailed reactions were displayed below:

$$C + H_2O \rightarrow H_2 + CO \tag{7}$$
$$CO + H_2O \rightarrow H_2 + CO_2 \tag{8}$$
$$C + CO_2 \rightarrow 2CO \tag{9}$$
$$2CO \rightarrow C + CO_2 \tag{10}$$
$$CH_4 + 2H_2O \rightarrow CO_2 + 3H_2 \tag{11}$$
$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO \tag{12}$$

The relative rates of these reactions, which are influenced by the reaction conditions (reaction temperature, *etc.*), determine the gaseous product composition. Therefore, the increasing reforming temperature would increase the absolute H$_2$ yield.
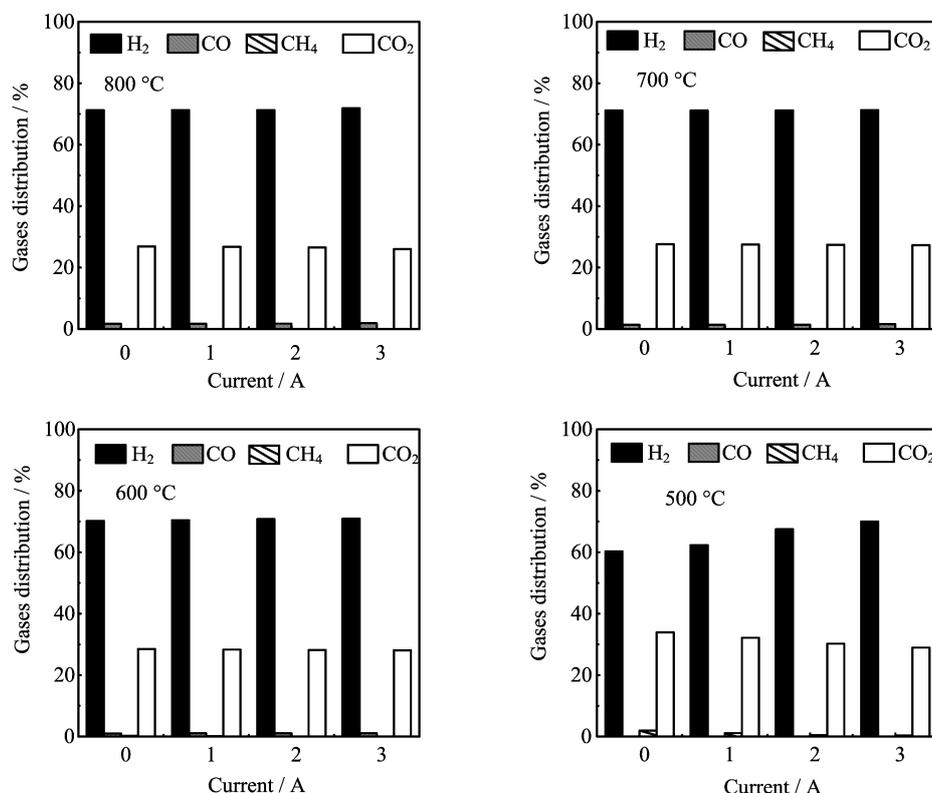
FIG. 5 Effect of current on distribution of main product gases in the reaction for producing hydrogen using crude bio-oil and biomass char. Conditions: T=500−800 °C, I=0−3 A, P=101 kPa, f=16.5 g/h, Ni-Al$_2$O$_3$ catalyst/biomass char=12 g/2.2 g, S/C=11, GHSV=6200 h^{-1}.

C. Influence of current

The influence of current over Ni-Al$_2$O$_3$ catalyst on absolute H$_2$ yield, carbon conversion and distribution of main product gases was investigated in electrochemical catalytic steam reforming for producing hydrogen from crude bio-oil and biomass char (I=0−3 A). Figure 4 shows the influence of current on absolute H$_2$ yield and carbon conversion. The absolute H$_2$ yield and carbon conversion remarkably increased with the increasing current at the same reforming temperature. At 800 °C and 3 A, the absolute H$_2$ yield was 110.9 g H$_2$/kg dry biomass and the carbon conversion was 88.3%. Figure 5 shows the influence of current on distribution of main product gases. The H$_2$ and CO content slightly increased with the increasing current, accompanied with the reduced CO$_2$ and CH$_4$ content. The promoted effect of the current for producing hydrogen from the crude bio-oil and biomass char could be qualitatively understood as follows. Firstly, the enhancement of the organic intermediates' reforming in the electrochemical steam reforming reaction process may partly arise from the higher temperature close to the electrified Ni-Cr wire. The temperature gradients in electrochemical steam reforming reaction (*i.e.*, inner heating mode) were higher than the conventional catalytic reforming (*i.e.*, outside heating mode) [25−27]. Particularly, the local temperature close to the electrified Ni-Cr wire was evidently higher than the average temperature, which may partly result in the higher activity of the catalyst close to the electrified Ni-Cr [25−27]. Secondly, the promotion by the current during electrochemical steam reforming reaction process may also originate from the catalyst's reduction caused by the thermal electrons. It is well known that when an electrified metal or a metal oxide is heated, electrons can boil off its surface, leading to thermal emission of electrons from surface (*i.e.*, thermal electron emission) [29]. It has been reported that thermal electrons on a metal or a metal oxide surface play an important role in the reduction process (*e.g.*, O$_2$+4e→2O^{2-}) [30]. The presence of the thermal electrons in the current-enhanced reforming process was experimentally confirmed by the anionic time of flight mass (TOF) and Faraday-plate methods in our previous work [25, 26]. These thermal electrons contributed to an additional reduction from the oxide states into the metallic states, leading to the enhancement of the catalytic activity. Finally, the promoting effects of the current may be partly attributed to the enhancement of the decomposition and reforming of the organic intermediates during electrochemical steam reforming reaction via the thermal electrons. The thermal electrons can cause the dissociation of the oxygenated organic compounds on the catalyst surface, which was confirmed by
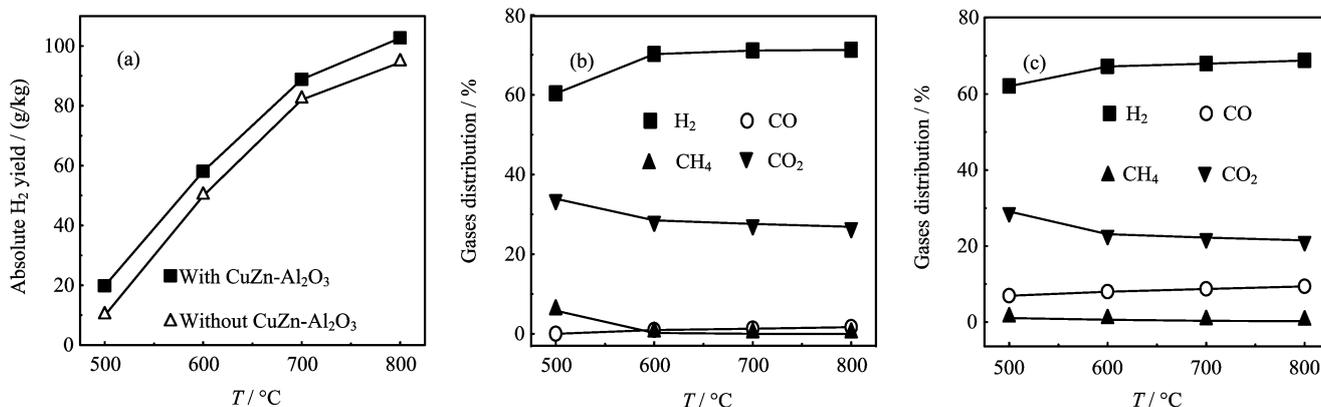
FIG. 6 Effect of the CuZn-Al$_2$O$_3$ catalyst on (a) the absolute H$_2$ yield, (b) and (c) distribution of the main product gases in the reaction for producing hydrogen using crude bio-oil and biomass char. Conditions: T=500−800 °C, P=101 kPa, f=16.5 g/h, Ni-Al$_2$O$_3$ catalyst/biomass char=12 g/2.2 g, S/C=11, GHSV=6200 h^{-1}.

using C$_2$H$_5$OH [26] and HAc [27] as model compounds. The dissociations of the oxygenated organic compounds lead to form small unstable fragments and some active radicals (*e.g.*, OH and CH), which may be very useful for prompting the reforming reactions [31].

D. Influence of CuZn-Al$_2$O$_3$ catalyst

Figure 6 shows the influence of adding the water-gas shift bed on the absolute H$_2$ yield and the distribution of main product gases. At the same reforming temperature, employing the water-gas shift catalyst, the absolute H$_2$ yield was higher than that only in the reforming bed. The absolute H$_2$ yield was 102.6 g H$_2$/kg dry biomass in the dual fixed bed reaction system at 800 °C. But without water-gas shift bed, the absolute H$_2$ yield decreased to 94.5 g H$_2$/kg dry biomass at the same reforming temperature. Figure 6 (b) and (c) show the influences of the water-gas shift catalyst on the distribution of main product gases. The H$_2$ and CO$_2$ contents were 71.2% and 26.8% with water-gas shift bed, while those were 68.8% and 21.5% only in the reforming bed at 800 °C. It is because that the water-gas shift catalyst could shift CO to CO$_2$ (Eq.(2)). In the meantime, the water-gas shift catalyst would shift H$_2$O to H$_2$. Thus, employing the water-gas shift bed would increase the H$_2$ and CO$_2$ content in product gases. Consequently, the absolute H$_2$ yield would be increased, but the carbon conversion would be almost the same.

IV. CONCLUSION

The present work provided an efficient approach for production of hydrogen by using crude bio-oil and biomass char in the dual fixed-bed system over the Ni-Al$_2$O$_3$ and CuZn-Al$_2$O$_3$ catalysts. The absolute hydrogen yield was increased by adding biomass char. Both the reforming temperature and current over the catalyst

promoted hydrogen production from the conversion of bio-oil and biomass char. The promotion of the current over the catalyst was due to the non-uniform temperature distribution in the catalytic bed and the role of the thermal electrons originating from the electrified wire. The CuZn-Al$_2$O$_3$ catalyst reduces the CO content in the product gases and increases the absolute H$_2$ yield. The max absolute H$_2$ yield reaches 110.9 g H$_2$/(1 kg dry biomass) with a gas products distribution of 72%H$_2$, 26%CO$_2$, and 1.9%CO.

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