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Maximum Hydrogen Production by Autothermal Steam Reforming of Bio-oil With NiCuZnAl Catalyst

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Autothermal steam reforming (ATR) of bio-oil, which couples the endothermic steam reforming reaction with the exothermic partial oxidation, offers many advantages from a technical and economic point of view. Effective production of hydrogen through ATR of bio-oil was performed at lower temperature with NiCuZnAl catalyst. The highest hydrogen yield from bio-oil reached 64.3% with a nearly complete bio-oil conversion at 600 °C, the ratio of steam to carbon fed (S/C) of 3 and the oxygen to carbon ratio (O/C) of 0.34. The reaction conditions in ATR including temperature, O/C, S/C and weight hourly space velocity can be used to control both hydrogen yield and products distribution. The comparison between the ATR and common steam reforming of bio-oil was studied. The mechanism of the ATR of bio-oil was also discussed.

Key words: Hydrogen, Bio-oil, Autothermal steam reforming, NiCuZnAl catalyst

I. INTRODUCTION

Hydrogen is an important raw material for chemical industry and has potential applications in transportation and production of electricity with fuel cell systems [1, 2]. Currently, most of industrial hydrogen is primarily produced via steam reforming of natural gas and oil-derived naphtha, partial oxidation of heavy oil residues, or coal gasification [3−5]. All these processes utilize fossil resources and produce a large amount of CO_2 that is believed to account for at least half of the anthropogenic greenhouse gas, which leads to global warming, climate change, and ocean acidification. Utilization of biomass as hydrogen resource is a method for suppressing greenhouse gas emission [6−9].

Various technical pathways can be used for the production of hydrogen from biomass, *i.e.*, anaerobic digestion, fermentation, metabolic processing, high pressure supercritical conversion, gasification, and pyrolysis [10−12]. Among them gasification and pyrolysis appear to be the most feasible. The combination of fast pyrolysis of biomass followed by steam reforming (SR) of the produced bio-oil has attracted considerable attention of the research community, as one of the most promising and economically viable methods for hydrogen production. Bio-oil has certain advantages such as higher energy density than biomass, easy storage and transportation, and flexibility to be used either as a re-

newable liquid fuel or for the production of chemicals [13−15].

One of the challenges of reforming process is that it consumes a great deal of energy. The concept of autothermal reforming (ATR) which is industrially practiced for methane SR, even though not new, attracts a lot of research interests for a variety of hydrocarbons, oxygenated, *etc.* [16]. ATR offers many advantages from a technical and economic point of view. It is a combination of oxidation and SR. Oxidation acts as an internal heat source that supplies thermal energy to the endothermic SR. Therefore, the ATR reaction can start quickly and continue without an additional/external heat supply. Moreover, the combination of these reactions can improve the reactor temperature control and reduce the formation of hot spots, avoiding catalyst deactivation by sintering or carbon deposition. These advantages make ATR the technology of choice for hydrogen production [17]. The method of autothermal reforming has been widely used for hydrogen production, *e.g.* autothermal reformation of methanol [18−21], hydrocarbons [22−25], and DME [26].

As mentioned above, there is considerable research on the autothermal reforming of methanol and hydrocarbons. However, the number of literatures directly related to production of hydrogen from bio-oil is quite small. Lemonidou *et al.* had reported autothermal reformation of model compounds of bio-oil and studied the effect of temperature, pressure and S/C (the ratio of steam to carbon fed) [17]. They found that temperature increase favored the formation of hydrogen up to 900 K where maximum concentration of hydrogen was attained and best results concerning hydrogen yield

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were attained at atmospheric pressure. Kechagiopoulos *et al.* had reported the performance of aqueous phase of bio-oil over Ni/olivine catalysts in a spouted bed reactor [27]. They reported that the implementation of the spouted bed reactor configuration, modified by the use of an injection nozzle, was proven successful, resulting in efficient processing of the organic model compounds. Coke formation, a major problem encountered in most reforming processes, was drastically limited owing to the favorable hydrodynamics of the spouted bed. Schmidt *et al.* had researched the effect of the properties of noble metal catalyst on the reaction [28, 29]. They gave a guide of reaction mechanism over noble metal catalysts.

Our lab has paid attention on the fast pyrolysis of biomass, the production of hydrogen or bio-syngas from the volatile fraction of the bio-oil and its model compounds and the synthesis of liquid bio-fuels such as gasoline and diesel *etc.* [30−33]. We studied various catalysts in the operation and found the NiCuZnAl catalyst could reach high hydrogen yield at relative lower temperature. In this work, we studied the autothermal steam reformation of bio-oil with NiCuZnAl catalyst at different temperature, S/C, and weight hourly space velocity (WHSV).

II. EXPERIMENTS

A. Feedstock

Bio-oil was produced by the fast pyrolysis of biomass in a circulating fluidized bed with a capacity of 120 kg/h of oil in our Lab. The main elemental composition of bio-oil feedstock derived from fast pyrolysis of straw stalk is 42.3%C, 7.9%H, and 49.4%O. Water content in the bio-oil is about 24.4%. The chemical formula of the oxygenated organic compounds of the bio-oil feed can be expressed as $CH_{2.12}O_{0.89}$.

B. Catalyst preparation and characterization

The NiCuZnAl catalyst was prepared by the co-precipitation method with selected Ni:Cu:Zn:Al molar ratio of 2:1:1:2 at a constant pH (9.0±0.2) using respective metal nitrates as precursors and a mixture of NaOH (1 mol/L) and Na_2CO_3 (1 mol/L) as precipitants. The precipitate was filtrated and washed to the neutral pH=7 and then dried in an oven at 120 °C for 8 h. Finally, the catalyst precursors was heated to 450 °C at a heating rate of 2 °C/min in air and calcined at 450 °C for 5 h.

The prepared catalysts were investigated by the XRD (X-ray diffraction), XPS (X-ray photoelectron spectroscopy), the N_2 physisorption and TGA (Thermal gravimetric analysis) method. The metallic contents in the prepared catalysts were measured by induc-

tively coupled plasma and atomic emission spectroscopy (ICP/AES, Atom scan Advantage of Thermo Jarrell Ash Corporation, USA). According to the ICP/AES, a trace amount of sodium element was observed in the prepared catalysts (about 0.26%). XRD measurements were employed to investigate the diffraction structure changes of the catalysts. XRD patterns of the catalysts were recorded on an X'pert Pro Philips diffractrometer, using a Cu Kα radiation. The surface elements and their states were analyzed by XPS. The XPS measurements were performed on an ESCALAB-250 (Thermo-VG Scientific, USA) spectrometer with Al Kα (1486.6 eV) irradiation source. The normalized XPS intensities, which are proportional to the concentrations of the corresponding elements in the surface layer, were determined as the integrated peak area divided by their corresponding sensitivity factor. The C1s peak at 284.6 eV was generally used as a calibration standard for determining the peaks' position and the elemental concentration. The Brunauer-Emmett-Teller (BET) surface area S_{BET} and pore volume (PV) was determined by the N_2 physisorption at −196 °C using a COULTER SA 3100 analyzer. TGA was carried out with a Q5000 TGA system (TA Instruments). The sample temperature was programmed from room temperature to 1000 °C at 10 °C/min. The S_{BET} and PV of fresh NiCuZnAl catalyst are 210.0 m²/g and 0.50 cm³/g, which evaluated from N_2 adsorption-desorption isotherms. And the average granule size d_{XRD} estimating from the peaks of XRD by the Scherrer equation is 11.4 nm.

C. Experimental setup and product analysis

The production of hydrogen from the autothermal steam reforming of bio-oil was carried out in the continuous-flowing systems, using a quartz fixed-bed reactor under atmospheric pressure. This system consists of a quartz tube reactor (inner diameter: 30 mm; length: 400 mm) with a reactant preheating system, a gas feed system, a liquid feeding pump, heaters and temperature control system, a condenser and an on-line gas analysis unit, which has been described in detail previously [34, 35]. Sieved NiCuZnAl catalyst powders (60−80 mesh) were held in the reactor by quartz beads. The liquid reactants were fed into the reactor using a multisyringe pump (TS2-60, Baoding Longer Precision Pump). The steam amount originating from a steam generator was adjusted by the mass flow controller. Before the reactions, the reactor was flushed by argon with the flow rate of 30 sccm for 1 h at the room temperature.

In this work, we performed and compared the bio-oil reforming tests with following three modes, *i.e.*, common SR, autothermal steam reforming with the reactants preheating (ATR-I), and complete autothermal steam reforming without the reactants preheating (ATR-II). For SR mode, the catalyst bed was homo-
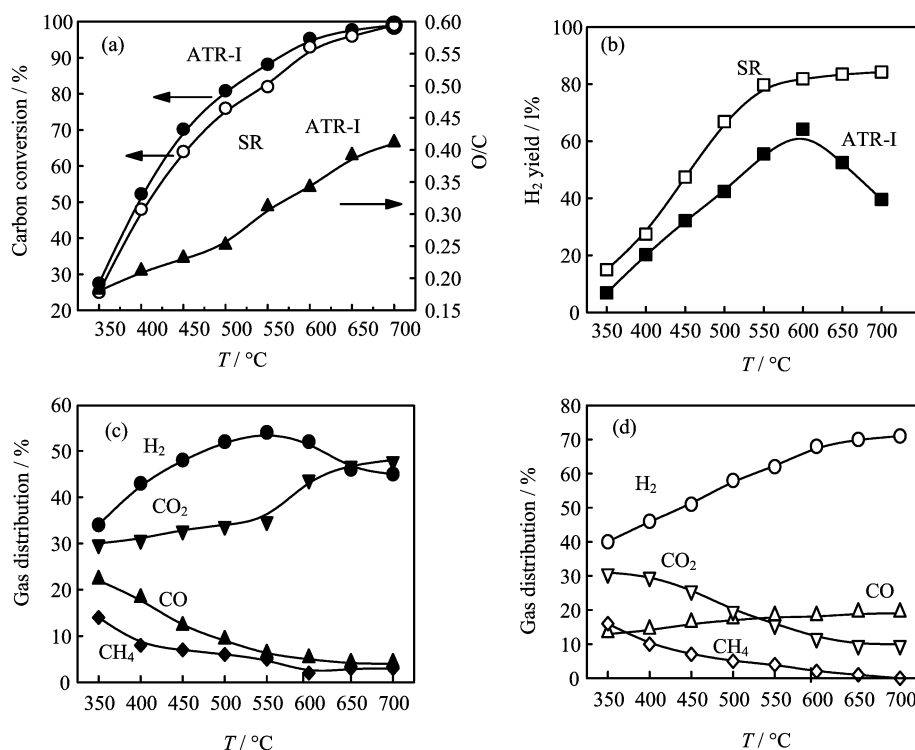
FIG. 1 Effect of temperature on production of hydrogen from ATR-I and SR of bio-oil over the NiCuZnAl catalyst. (a) Carbon conversion. (b) Hydrogen yield. (c) ATR-I products distribution. (d) SR products distribution. Conditions: S/C=3, WHSV=1.5 h^{-1}, preheating temperature 300 °C.

geneously heated by an outside heating furnace. For ATR-I mode, the power source of the outside furnace was shut off, and the reactants were first preheated to 300 °C before entering the catalytic bed reactor. The reaction temperature is a dependent variable, which offered by the exothermic partial oxidation of bio-oil under a controlled oxygen to carbon ratio. For ATR-II mode, the power source of the outside furnace was shut off and the reactants at the room temperature was directly fed into the catalytic bed reactor. The whole heat duty was provided by the oxidation of bio-oil. The gaseous products were analyzed using an on-line GC equipped with two detectors, a TCD for analysis of H_2, CO, CH_4, and CO_2 separated on TDX-01 column, and a flame ionization detector (FID) for gaseous hydrocarbons separated on a Porapak-Q column. The process performance was studied by measuring the carbon conversion of bio-oil to gases $C_{conv.}$, the hydrogen yield Y_{H_2}, and distribution of product gases. The carbon conversion is calculated according to Eq.(1) and the hydrogen yield is calculated according to Eq.(2).

$$C_{conv.} = \frac{x_{inC} - x_{outC}}{x_{inC}} \times 100\% \qquad (1)$$

$$Y_{H_2} = \frac{x_{H_2}}{y_{H_2}} \times 100\% \qquad (2)$$

where x_{inC} and x_{outC} are the carbon moles of feed in and feed out, and x_{H_2} and y_{H_2} are moles of H_2 obtained

and H_2 in stoichiometric potential. All the tests were repeated three times. The difference for each replicate generally is less than 10% and the mass balance of the fed biomass is over 90%. The reported data are the mean values of three trials.

III. RESULTS AND DISCUSSION

A. Effect of temperature on ASR of bio-oil

The ATR reactions for bio-oil were investigated with the NiCuZnAl catalyst in a range of temperatures of 350−700 °C, S/C ratio of 1−6, and WHSV of 1−5 h^{-1} at atmospheric pressure. To maximize hydrogen production, the reactants were first preheated to 300 °C before entering the catalytic bed reactor (ATR-I mode). Figure 1 shows the bio-oil conversion, hydrogen yield and the gas products distribution as a function of temperature during the ATR reactions of bio-oil. The respective results that obtained from the common SR by external heating with an anaerobic condition also presented to serve as a contrast. In the ATR process, temperature of the reforming reactions is a dependent variable which is controlled by the oxygen to carbon ratio. The key operating parameter of the autothermal system is the necessary amount of oxygen to minimize the heat duty of the reactor. The values of O/C which are neces-
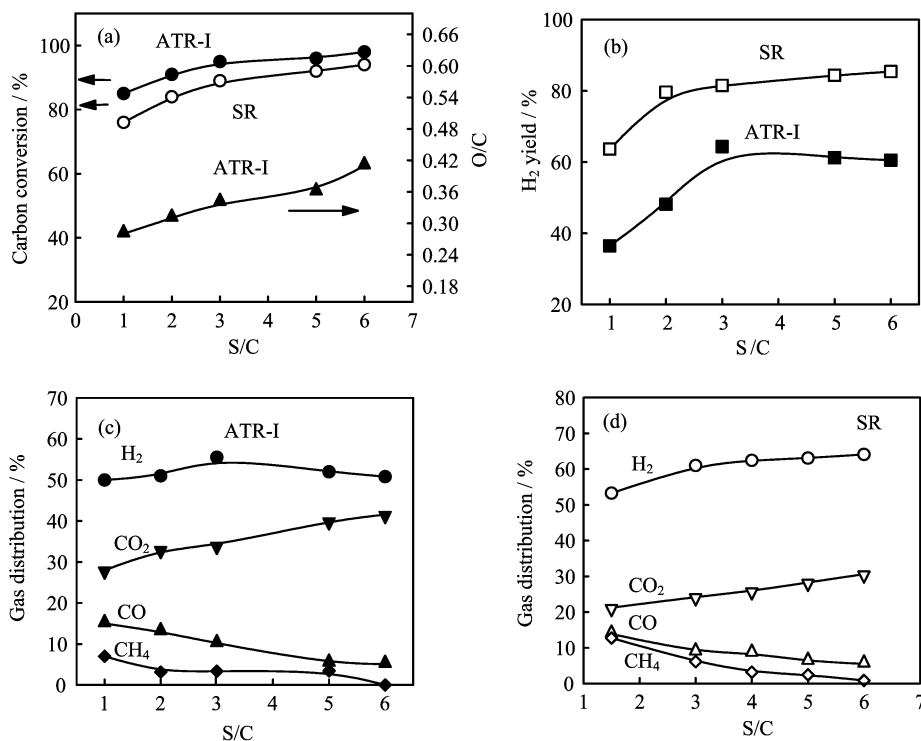
FIG. 2 Effect of S/C on production of hydrogen from ATR-I and SR of bio-oil over the NiCuZnAl catalyst. (a) Carbon conversion. (b) Hydrogen yield. (c) ATR-I products distribution. (d) SR products distribution. Conditions: T=600 °C, WHSV=1.5 h^{-1}, preheating temperature 300 °C.

sary for the autothermal conditions in the temperature range 350−700 °C, varied from 0.18 to 0.42.

The total bio-oil conversion in ATR-I increased from 27.5% to 95.3% with increasing temperature from 350 °C to 600 °C, and was close to an almost complete conversion at 650 °C (Fig.1(a)). This indicates that high temperature is more favorable to the reforming and catalytic oxidation reactions of the oxygenated compounds in the bio-oil. It is noticed that the bio-oil transformation in ATR-I proceeds faster than that occurring in SR. However, the hydrogen yield derived from the autothermal steam reforming is obviously lower than the contrast group from the common SR (Fig.1(b)). The hydrogen yield in ATR-I goes through a maximum of 64.3% near 600 °C. Further increasing temperature to 700°C significantly reduced the hydrogen yield to 39.6%. The decrease in the hydrogen production in ATR-I, as compared to that derived from SR, is mainly attributed to that part of bio-oil fed consumed by the oxidation for the heat generation. The hydrogen combustion reaction may also occur at high temperature region, and further exacerbate the reduction of hydrogen yield.

With regard to the gas products distribution in ATR-I (Fig.1(c)), the main products decrease in the following order: H_2>CO_2>CO>CH_4. The hydrogen concentration presents a maximum value of 54% around 550 °C. The final molar fraction of hydrogen in the gas mixture

in ATR-I is determined by the thermodynamic equilibrium of complex reaction process, including the reforming, oxidation, decomposition and the water gas shift reactions at the given condition. The increase in the CO_2 fraction at high temperature indicates that the oxidation reaction of bio-oil is aggravated, because the higher oxygen to carbon ratio is required to achieve the autothermal condition. Methane dominates at lower temperatures for the autothermal steam reforming of bio-oil, and appears a sharp reduction through methane SR when temperature increases.

B. Effect of steam to carbon ratio on ATR of bio-oil

The S/C is another important parameter that determines to a great extent of hydrogen production and also have an influence on the coke formation under bio-oil reforming. Figure 2 shows the effect of S/C on the production of hydrogen from the autothermal steam reforming of bio-oil over the NiCuZnAl catalyst at T=600 °C, S/C=1−6 and WHSV=1.5 h^{-1}. The respective results that obtained from the common SR by external heating with an anaerobic condition also presented to serve as a contrast. The total bio-oil conversion in ATR-I increased from 85.1% to 98.2% with increasing S/C from 1 to 6. The hydrogen yield in the ASR of bio-oil went through a maximum of 64.3% with an S/C of 3, and no apparent effect on hydrogen pro-
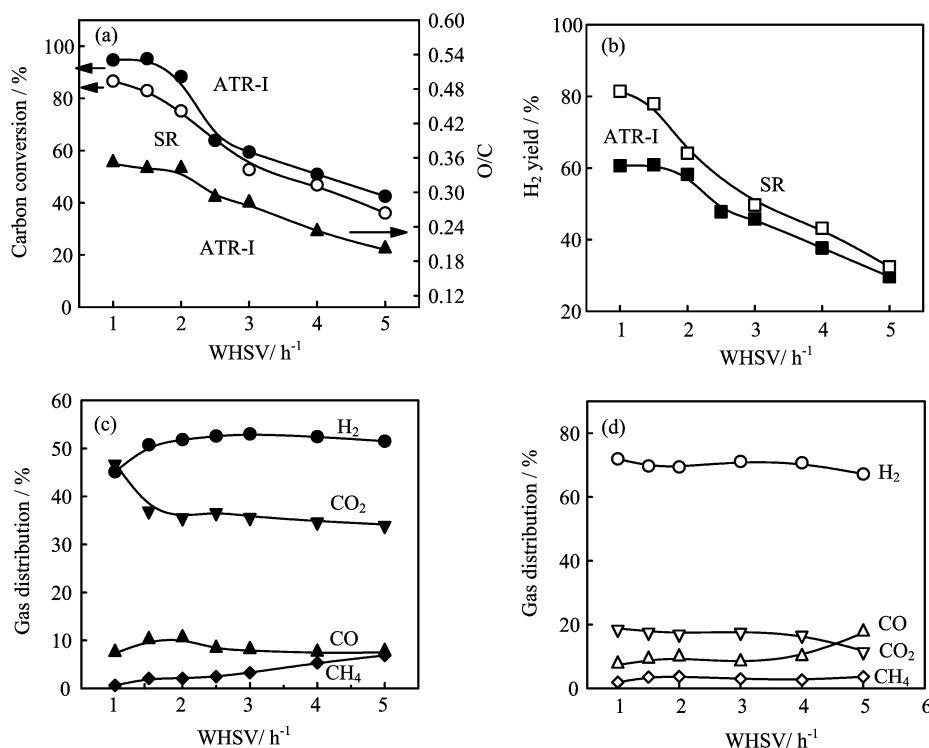
FIG. 3 Effect of WHSV on production of hydrogen from ATR-I and SR of bio-oil over the NiCuZnAl catalyst. (a) Carbon conversion. (b) Hydrogen yield. (c) ATR-I products distribution. (d) SR products distribution. Conditions: T=600 °C, S/C=3, preheating temperature 300 °C, WHSV=1−5 h^{-1}. ATR-I: O/C=0.35−0.21.

duction was observed by further increasing S/C over 3. This indicates that higher S/C is more favorable to the reforming of the oxygenated compounds in the bio-oil as well as the water gas shift reaction. Also, there is a significant influence of S/C on the selectivity of the carbon-containing products, $i.e.$, CO, CO_2, and CH_4. It was found that the selectivity of CO steadily decreased with increasing S/C, accompanied by a synchronous increase in the CO_2 selectivity. This result indicates that the water gas shift equilibrium is shifted to the right due to the increase of H_2O concentration. Methane content was also significantly inhibited through enhancing the methane reforming with increasing S/C. It should be pointed out that increasing S/C will increase the heat duty as well as the necessary amount of oxygen to neutralize the reactions in the ASR system. Thus, S/C should minimize as far as possible.

C. Effect of weight hourly space velocity on ATR of bio-oil

Figure 3 shows the production of hydrogen from the ATR-I as a function of WHSV. The respective results that obtained from the common SR by external heating with an anaerobic condition also presented to serve as a contrast. WHSV is defined as the mass flow rate of the feed divided by the mass of the catalyst in the reactor. With the increase in WHSV from 1 h^{-1} to 5 h^{-1},

the bio-oil conversion steeply reduced from 94.7% to 42.5%. The hydrogen yield followed a similar trend as the bio-oil conversion. Increasing WHSV also resulted in the decrease in the CO_2 selectivity, accompanied by the notable increase in the CO and CH_4 selectivity.

In particular, the methane amount in the ATR of bio-oil obviously ascended in the case of higher WHSV. The increase of space velocity generally shortens the reactants residence time in the catalyst bed, leading to the decrease in the bio-oil conversion as well as the hydrogen yield. The increase of selectivity of CO and CH_4 with increasing WHSV may be attributed that a shorter reaction time will slow down the reforming and the water gas shift reaction.

D. ATR without the preheating of the reactants

In the real production hydrogen process using bio-oil, the whole energy consumption should include two parts, $i.e.$, the first part for the endothermic reforming reaction and the second energy consumer for the preheating of the reactants. We tested the complete ATR process, in which the total energy is taken into account expressed as the total amount of oxygen needed for the reforming reaction and the preheating of the reactants. Figure 4 presents the bio-oil conversion, hydrogen yield, and the gas products distribution as a function of temperature during the complete ATR of bio-oil. Without
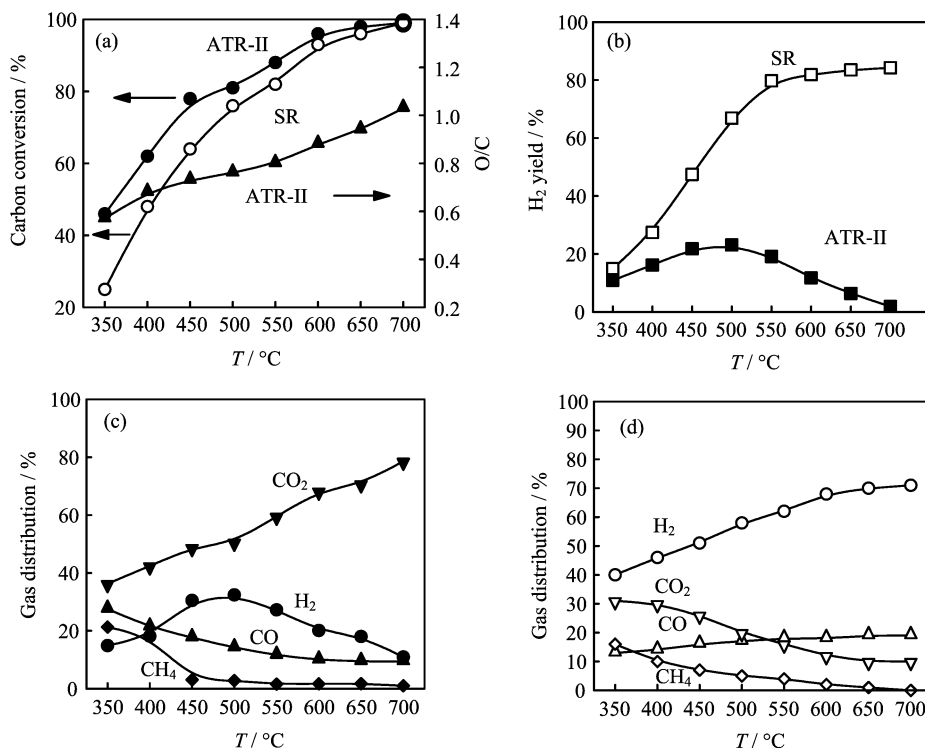
FIG. 4 Effect of temperature on production of hydrogen from ATR-II and SR of bio-oil over the NiCuZnAl catalyst. (a) Carbon conversion. (b) Hydrogen yield. (c) ATR-II products distribution. (d) SR products distribution. Conditions: S/C=3, WHSV=1.5 h^{-1}, no preheating.

the preheating of the reactants, the oxygen to carbon ratios required for the heat duty in the corresponding reaction temperature of 350−700 °C significantly increased to the standard of 0.55−1.05, which was much higher than the level of 0.18−0.42 in ATR with the preheating of the reactants at 300 °C. More particularly, the amount of hydrogen produced in the complete ATR process was drastically reduced compared with SR, implying that most of the bio-oil was consumed for the oxidation reactions to cover the energy demands. Maximum hydrogen yield was below 20% at 350−500 °C. A further increase of the reaction temperature had a detrimental effect on the hydrogen yield, as much higher amounts of fuel have to be allocated to the combustion for heat. This is demonstrated by the increased the oxygen to carbon ratios that are required to cover the energy requirements (Fig.4). In addition, the combustion reaction of hydrogen may also occur at high temperature and high oxygen content, and further reduce the hydrogen yield. In the ATR of bio-oil with the preheating of the reactants at 300 °C, hydrogen is the major product with a content of about 30%−50%. For the complete ATR process, however, CO_2 becomes the main product (35%−80%) observed in the effluent carbonaceous compounds. Under the condition of high temperature and high oxygen content, a large amount of CO_2 generates through the bio-oil oxidation with water as a by-product.

E. Catalyst stability in ATR of bio-oil

As shown in Fig.5, the catalyst stability in the ATR of bio-oil was tested as a function of the time on stream at T=550 °C, S/C=3.0, WHSV=1.5 h^{-1}. A slow decrease in the bio-oil conversion and hydrogen yield had been observed in a 30 h time on stream period. The bio-oil conversion declined from the initial value about 84.8% to 62.4%. The yield of hydrogen gradually decreased from 62.1% to 35.2% for 30 h. The selectivity towards CO and CH_4 slightly increased, indicating that the decrease in the activity of the reforming and the water gas shift reaction with the used catalyst. The decrease in the catalyst activity is mainly attributed to the carbon deposition on the catalysts in the ATR of bio-oil. Furthermore, the rate of the carbon deposition on the catalyst surface was characterized by the TGA measurements, being about 1.5 mg C/(g$_{catal}$h) in the ATR of bio-oil.

F. Reaction pathways and maximum hydrogen production in ATR

Bio-oil produced through the fast pyrolysis of biomass is a complex mixture of several hundreds of oxygenated organic compounds including acids, alcohols, aldehydes, ketones, substituted phenolics and other oxygenates.
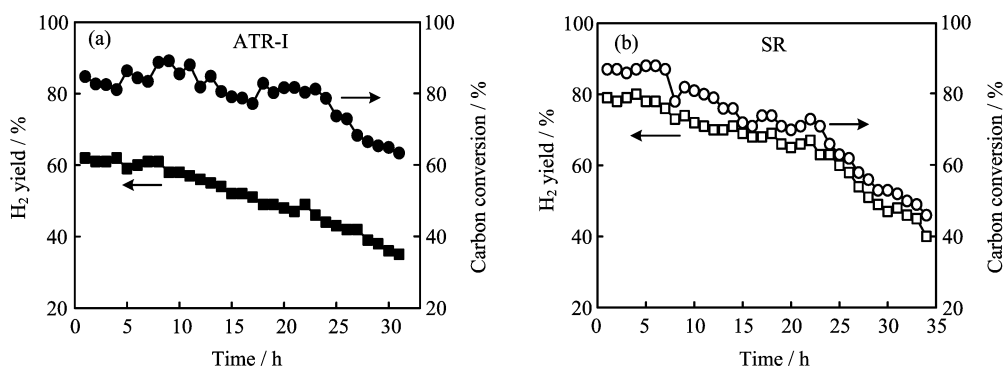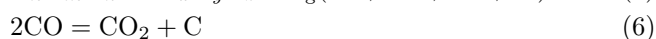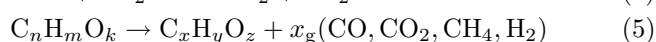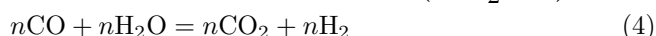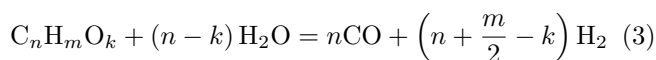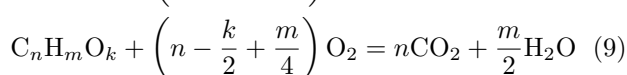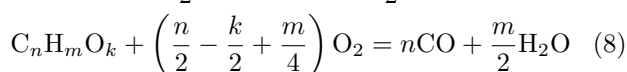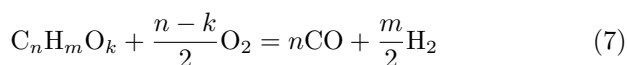
FIG. 5 Effect of time on stream on the carbon conversion and hydrogen yield over the NiCuZnAl catalyst. Conditions: T=550 °C, S/C=3, WHSV=1.5 h^{-1}, preheating temperature 300 °C.

According to study on production of hydrogen from bio-oil and its model compounds (*e.g.* alcohols, acetic acid, acetone, toluene and aromatics) by our group and other research groups [36], the steam reforming of bio-oil is mainly determined by the ability of a catalyst to catalyze the steam reforming reactions of the oxygenated organic compounds ($C_nH_mO_k$) in bio-oil (Eq.(3)), and the water-shift reaction (Eq.(4)). In the case of the moderate and high temperatures, partial thermal decomposition of bio-oil (Eq.(5)) and the Boudouard reaction (Eq.(6)) may simultaneously occur.

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

$$nCO + nH_2O = nCO_2 + nH_2 \quad (4)$$

$$C_nH_mO_k \rightarrow C_xH_yO_z + x_g(CO, CO_2, CH_4, H_2) \quad (5)$$

$$2CO = CO_2 + C \quad (6)$$

where x_g is gaseous small molecule. With regard to the ATR of bio-oil, the bio-oil oxidation that provides heat to the system may include several reactions depending on the reaction conditions (Eqs. (7)−(9)):

$$C_nH_mO_k + \frac{n - k}{2}O_2 = nCO + \frac{m}{2}H_2 \quad (7)$$

$$C_nH_mO_k + \left(\frac{n}{2} - \frac{k}{2} + \frac{m}{4}\right) O_2 = nCO + \frac{m}{2}H_2O \quad (8)$$

$$C_nH_mO_k + \left(n - \frac{k}{2} + \frac{m}{4}\right) O_2 = nCO_2 + \frac{m}{2}H_2O \quad (9)$$

In present work, the main products observed from the ATR of bio-oil with the preheating of the reactants at 300 °C and the NiCuZnAl catalyst are H_2 and CO_2, together with a small amount of CO and CH_4. The highest hydrogen yield of 64.3% with a bio-oil conversion of 95.3% was achieved in the ATR of bio-oil at T=600 °C, S/C=3, WHSV=1.5 h^{-1}, O/C=0.34. The maximum hydrogen yield from the ATR of bio-oil was slightly lower than the value of 83.5% from the SR of bio-oil at T=650 °C, S/C=3, WHSV=1.5 h^{-1}. The ATR-1mainly combined the simple reforming process

with the oxidation process. The oxidation and reforming reactions seem to act a competing relationship, considering that the trends of the product distribution observed in ATR and SR are quite different. Especially, the oxidation reaction of Eq.(9) should be suppressed as far as possible by the control of reaction temperature and oxygen content since it will cause the large formation of CO_2 and water. Carbon monoxide and methane are also considered undesirable products in production hydrogen process. Carbon monoxide affects the overall size of the facilities, especially the water gas shift reactor, and methane contains hydrogen, decreasing thus the overall hydrogen production. The higher the ratio of steam to fuel can increase the higher hydrogen production by shifting the equilibrium of reforming reaction and the water gas shift. However, the energy consumption and the size of the units increase with increasing steam flows. Taking into account all the factors mentioned above, the optimum operating conditions for the ATR-I may control at T=500−600 °C, S/C=2−3, and O/C=0.2−0.3.

IV. CONCLUSION

This work reported ATR of bio-oil at lower temperature with NiCuZnAl catalyst. The highest hydrogen yield from bio-oil reached 64.3% with a nearly complete bio-oil conversion. The reaction conditions in ATR including temperature, oxygen to carbon ratio, the ratio of steam to carbon fed and weight hourly space velocity can be used to control both hydrogen yield and products distribution. To maximum hydrogen production, the optimum operating conditions for the ATR of bio-oil should control at T=500−600 °C, S/C=2−3, and O/C=0.2−0.3. The ATR results in the decrease of hydrogen yield around 20% lower than the yield by SR, because part of the organic feed is consumed in the combustion reaction. The oxidation and reforming reactions seem to act a competing relationship, considering that the trends of the product distribution observed in ATR and SR are quite different. ATR of bio-oil may

potentially provide a promising route for reducing energy consumption and cost the production of hydrogen using renewable biomass.

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