Hydrogen production by steam reforming of acetic acid and bio-oil using Ni/γ-Al_2O_3 catalysts

Li Yanmei[1,2], Fu Peng[1,2*], Yi Weiming[1,2], Bai Xueyuan[1,2*]

(1. *School of Agricultural and Food Engineering, Shandong University of Technology, Zibo, Shandong 255049, China*;
2. *Shandong Research Center of Engineering and Technology for Clean Energy, Zibo, Shandong 255049, China*)

Abstract: Hydrogen production from steam reforming of bio-oil and acetic acid using Ni/γ-Al_2O_3 catalyst was studied in a laboratory-scale fixed bed reactor. This study selected different Ni loadings (16.8% and 30.5%) in Ni/γ-Al_2O_3 catalysts and reaction temperatures (500°C, 600°C and 700°C) as variables to optimize the hydrogen yield and selectivity of gases formed. Experiments were carried out in an isothermal manner. The catalysts were prepared on wet impregnation of a γ-Al_2O_3 which supported with two different Ni loadings. The principal gases generated were H_2, CO, CO_2 and CH_4. The results from steam reforming of acetic acid showed that the yield and selectivity of hydrogen using the catalyst with 30.5% Ni were significantly higher than that with 16.8% Ni. The results showed that the most favorable temperature for hydrogen production was 600°C, and the steam reforming of bio-oil using Ni/γ-Al_2O_3 catalyst with 30.5% Ni showed that the yields and selectivity of H_2 and CO_2 increased with the temperature increasing while CH_4 and CO selectivity decreased. These results showed that the most favorable temperature for hydrogen production from bio-oil using 30.5% Ni/γ-Al_2O_3 was 600°C, at which hydrogen yield was at its maximum of 65%.

Keywords: hydrogen, bio-oil, Ni/γ-Al_2O_3 catalyst, steam reforming, acetic acid
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1 Introduction

With the rapid increase of energy consumption, burning of fossil fuels could cause global warming and led to the issue of climate change in the recent decades[1,2]. The demand for substitute energy sources becomes a major concern of the economy. Biomass, one of the possible alternative energy sources, is a renewable and CO_2-neutral fuel carbon source. Biomass can be converted into several types of liquid or gaseous products, and bio-oil can be converted into hydrogen by catalytic steam reforming (SR)[3]. The hydrogen is recognized as a clean fuel and energy carrier and will certainly play an important role in the future global economy[4]. It is, however, a fact that current hydrogen production is substantial, between 38 and 53 million metric tons worldwide as of 2010[5,6]. According to the statistics of US Department of Energy, around 95% of the current US hydrogen production which provide about half hydrogen supply in the world[7], is produced from fossil such as natural gas, naphtha and coal, and the statistical data are not much different in the rest of the world. Therefore, the SR of bio-oil derived from fast pyrolysis of biomass is a viable process for the production of hydrogen[8].

The conventional SR process is usually catalyzed by the group VIII metals and Ni. Nickel-based catalysts have

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Biographies: Li Yanmei, Graduate student, Research interests: agriculture engineering. Email: liyanmei0817@163.com; **Fu Peng**, Lecturer, Research interests: biomass pyrolysis and gasification technology. Email: fupeng@sdut.edu.cn; **Yi Weiming**, PhD, Professor, Research interests: biomass pyrolysis and gasification technology, Email: yiweiming@sdut.edu.cn.

***Corresponding author: Bai Xueyuan,** PhD, Professor, Research interests: biomass utilization technology. Address: Shandong Research Center of Engineering and Technology for Clean Energy, School of Agricultural and Food Engineering, Shandong University of Technology, No.12 Zhangzhou Road, Zhangdian District, Zibo, Shandong 255049, China. Tel/Fax: +86-533-2786158, Email: baixy@sdut.edu.cn.

been widely used for reforming of bio-oil due to its lower price and their high activity in the decomposition of oxygenated compounds, and some relevant studies have been conducted[9]. The Ni loading ranging from 5% (wt) to 30% (wt) has been investigated by different researchers for ethanol and acetic acid[10-13]. The robustness of the catalyst based on Ni guarantees operation over thousands of hours[14], but this metal leads to extensive coke formation in the case of the whole bio-oil. In the previous studies, Ni has been demonstrated the active species that catalyzed the reaction, and Ni loading had an effect on the catalytic reforming of the model compounds studied[15]. The support material is MgO, other basic oxides are Al_2O_3, calcium or magnesium aluminates[16]. Activated Al_2O_3 as a carrier of catalysts were widely used due to its porosity and greater surface area for adsorbing more active composition to meet catalytic requirements. The wet impregnation method was applied for the preparation of catalysts, by which the active metals were loaded onto the prepared catalyst support. The details of the wet impregnation are described elsewhere[17]. In catalytic SR reaction, the main problems of catalysts are not stable over longer periods of operation (>100 h) and has a short lifetime due to the carbon deposition. Catalysts prepared in this study should have higher catalytic activity and stability, and the preparation method should be convenient in application with low costs.

The SR of bio-oil is considered to be a sustainable route to hydrogen production from biomass. Bio-oil is a complex mixture, whose major components are oxygenated compounds such as alcohols, acids, aldehydes and ketones, as well as more complex carbohydrates and lignin derived materials[18]. Acetic acid is one of the major components in bio-oil; it has noninflammable or explosive nature than in methanol and ethanol and is a safe hydrogen carrier. Due to the complexity of bio-oil, some researchers have used model compounds as a substitute for bio-oil in their studies. Of these, acetic acid has been widely used for thermal analysis of catalytic SR.

The purpose of this study was to investigate catalytic SR of bio-oil for hydrogen production. The main focus will be on catalytic SR of bio-oil and model compound acetic acid using Ni/γ-Al_2O_3 catalysts under different temperatures and Ni loading in a laboratory-scale atmosphere fixed bed reactor, which in order to investigate how the reaction temperature and Ni loading effected on the yield and selectivity, as temperature is the most important parameter in catalytic SR of bio-oil. Gas releasing behaviors, yield and selectivity from the SR experiments will be also presented in details and suggestions to further investigations will be given.

2 Materials and methods

2.1 Materials

The bio-oil ($CH_{1.954}O_{0.841}$) used in this research was produced by fast pyrolysis of corn straw. Table 1 gives some physical and chemical properties of the bio-oil used. The main elemental composition of the bio-oil was carbon (C), hydrogen (H), nitrogen (N) and oxygen (O). The major chemical compounds in corn stalk fast pyrolysis bio-oil as determined by GC/MS were shown in Table 2. The major chemical compounds included 1-hydroxy-2-propanone, acetic acid, ethanol, 1,2-Ethanediol, 2-Methyl-2-cyclopenten-1-one, benzenediol, levoglucosan and phenols, etc.

Acetic acid (99%) were purchased from Yantai Chemical Reagent Co., Ltd. Aluminum oxide (γ-Al_2O_3) and nickel nitrate hexahydrate ($Ni(NO_3)_2\cdot 6H_2O$) were of high purity and purchased from Sinopharm Chemical Reagent Co., Ltd.

Table 1 The main properties of bio-oil derived from fast pyrolysis of corn stalk

Properties	
Ultimate analysis/% wt	
Carbon	43.80
Hydrogen	7.12
Nitrogen	0.42
Oxygen (by difference)	48.66
Water content/% wt	24.10
Density/$g\cdot cm^{-3}$	1.05
v/$MPa\cdot s$	1.90
pH	3.2
HHV/$MJ\cdot kg^{-1}$	17.6

2.2 Catalysts preparation

The γ-Al_2O_3 was first pretreated at 650°C for 6 h and then crushed to 20-30 meshes. Following a typical impregnation procedure, known amounts of $Ni(NO_3)_2\cdot 6H_2O$ was dissolved in deionised water and the prepared γ-Al_2O_3 was added to the solution. The obtained slurry was kept stirring at room temperature for 3 h and dried for 12 h in an oven at 105°C, finally calcined at 500°C for 3 h in a muffle furnace. ZSX100e type X-ray fluorescence spectrometer was applied to measure the Ni loading in the prepared catalysts, which can be used for the qualitative and quantitative analysis of most of the elements in the periodic table, even up to 100% of the element concentration also could be directly measured without dilution. Finally two Ni/γ-Al_2O_3 catalysts were obtained with Ni loading of 16.8% and 30.5%.

2.3 Experimental apparatus and procedure

The experimental apparatus is shown in Figure 1. It consisted of a cylindrical quartz tube reactor provided with a heating system, inlets for feeding the gases, bio-oil and model compounds and a Gas board-3100 gas analyzer as well as accessories to collect the gas samples. The heating system consisted of a tubular electric furnace and a power source, temperature being controlled automatically by a temperature controller. All experiments were carried out isothermally.

Table 2 Major chemical compounds in corn stalk fast pyrolysis bio-oil as determined by GC-MS

No.	RT/min	Compound name
1	5.044	Ethanol
2	9.433	Acetic acid
3	11.048	2-Propanone, 1-hydroxy-
4	15.358	1,2-Ethanediol
5	21.142	2-Furanmethanol
6	21.564	2-Propanone, 1-(acetyloxy)-
7	21.681	2-Cyclopenten-1-one, 2-methyl-
8	21.913	1,2-Ethanediol, monoacetate
9	22.507	Ethanone, 1-(2-furanyl)-
10	27.055	Butanoic acid, 4-hydroxy-
11	32.049	Phenol, 2-methoxy-
12	33.604	Phenol, 2-methyl-
13	33.953	2-Cyclopenten-1-one,3-ethyl-2-hydroxy-
14	34.296	Cyclobutanemethanol
15	37.215	Cyclopropyl carbinol
16	39.352	Phenol, 4-ethyl-
17	42.773	Xanthosine1,
18	45.313	2-Benzenediol
19	49.97	Hydroquinone
20	51.600	3,5-Dihydroxytoluene
21	58.650	1,6-Anhydro-á-D-glucopyranose (levoglucosan)

The catalysts were placed in middle of the quartz tube reactor which had an inner diameter of 10 mm and a length of 860 mm. Before the experiments, N_2 was used to purge the reaction tube at flow rate of 50 mL/min for 30 min, then catalysts were reduced by H_2 at flow rate of 50 mL/min for 3 h at 500°C. When the reduction was completed, the reactor was by N_2 ($\geqslant$99.995%) at the flow rate of 100 mL/min until the H_2 content$\approx$0 in the gas analyzer, and heated up to the desired temperature in the temperature range of 500-700°C. Acetic acid/Bio-oil and water were injected into the reactor by two high-pressure syringe pumps, which can achieve the required water to carbon ratio. During the reaction processes, gaseous products were filtered, condensed and dried, and finally, the compositions and contents of final gaseous products were analyzed and recorded by Gas board-3100 gas analyzer, which was equipped with the proprietary non-dispersive infrared gas sensor and thermal conductivity detector and could quantify H_2, CO, CO_2 and CH_4.

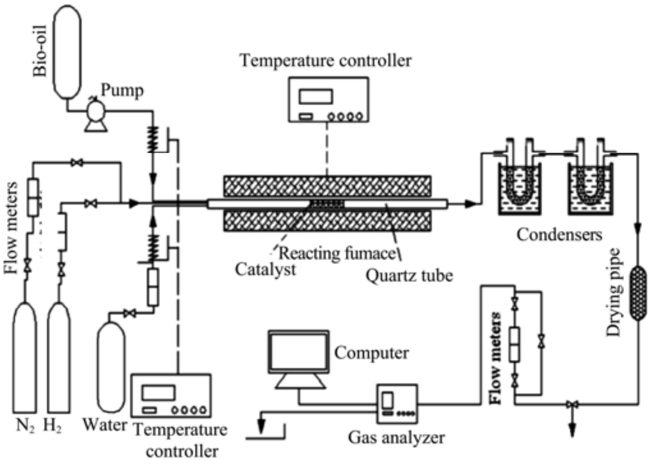


Figure 1 Schematic diagram of laboratory-scale apparatus used for catalytic steam reforming

2.4 Data analysis

The overall SR reaction may be represented as follows:

$$C_nH_mO_k + (2n-k)H_2O \xrightarrow{Catalyst} nCO_2 + (2n + \frac{m}{2} - k)H_2 \tag{1}$$

Reforming of acetic acid and bio-oil for hydrogen production can be summarized by the following reactions as discussed in Equations (2) and (3). In fact, a series of accompanied side reactions were involved in hydrogen production from SR, which was well discussed in literatures[19-24], mainly including thermal decomposition (Equations (4), (5) and (6)), carbon monoxide conversion (Equation (7)) and methanation reaction (Equations (8) and (9)) .

$$CH_3COOH + 2H_2O \xrightarrow{Catalyst} 2CO_2 + 4H_2 \quad (2)$$

$$CH_{1.954}O_{0.841} + 1.159H_2O \xrightarrow{Catalyst} CO_2 + 2.136H_2 \quad (3)$$

$$CH_3COOH \rightarrow 2CO + 2H_2 \quad (4)$$

$$CH_3COOH \rightarrow CH_4 + CO_2 \quad (5)$$

$$C_nH_mO_k \rightarrow C_xH_yO_z + gas(H_2 + H_2O + CO + CO_2 + CH_4, \cdots) + Coke \quad (6)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad (7)$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O \quad (8)$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad (9)$$

The S/C ratio was defined as the number of moles of total water fed to the moles of carbon in the feed (Equation (10)), which was 6:1 considered in the formula.

$$R = S/C = \frac{moles\,of\ total\,water\ fed}{moles\,of\ carbon\ fed} \times 100\% \quad (10)$$

The catalytic performances of the catalysts were evaluated in terms of H_2, CO, CO_2 and methane yields. Hydrogen yield ratio (Equation (11)) was defined as the moles of produced hydrogen in the actual effluent gas to the theoretical amount of hydrogen that can be obtained when complete reforming to CO_2 and H_2 occurs. CO, CO_2 and CH_4 yields were defined as the number of moles of gas formed per mole of carbon fed (Equation (12)). Terms of product selectivity were described in Equations (13) and (14).

$$H_2 \text{ yield} = \frac{\text{moles of } H_2 \text{ obtained}}{(2n + \frac{m}{2} - k) \text{ moles of cabonfed}/n} \times 100\% \quad (11)$$

$$\text{Yield of "}i\text{"} = \frac{\text{moles of gas "}i\text{" obtained}}{\text{moles of carbon in the feed}} \times 100\% \quad (12)$$

$$\text{Selectivity of } H_2 = \frac{\text{moles of hydrogen obtained}}{\text{moles of } H \text{ obtained in all gases}} \times 100\% \quad (13)$$

$$\text{Selectivity of "}i\text{"} = \frac{\text{moles of } C \text{ in gas "}i\text{" obtained}}{\text{moles of } C \text{ in all obtained gases}} \times 100\% \quad (14)$$

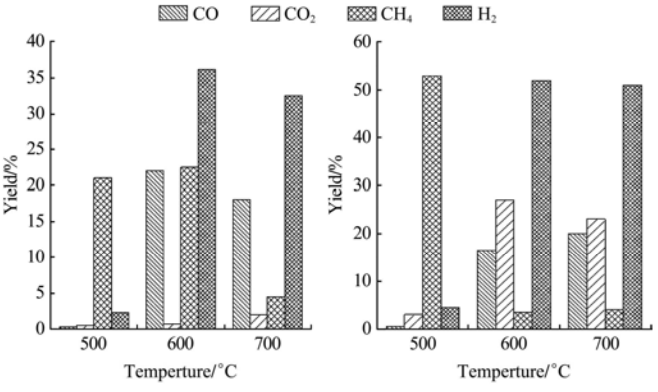
3 Results and discussion

3.1 SR of acetic acid

There were some valuable methods and data for hydrogen production from bio-oil by studying of SR of acetic acid[25]. Based on results from thermodynamic analyses of SR of acetic acid for hydrogen production, larger gaseous production was obtained at the temperature range of 400-650°C. Therefore, catalysts were evaluated from 500°C, 600°C and 700°C in the catalytic SR of acetic acid as the model compound of bio-oil.

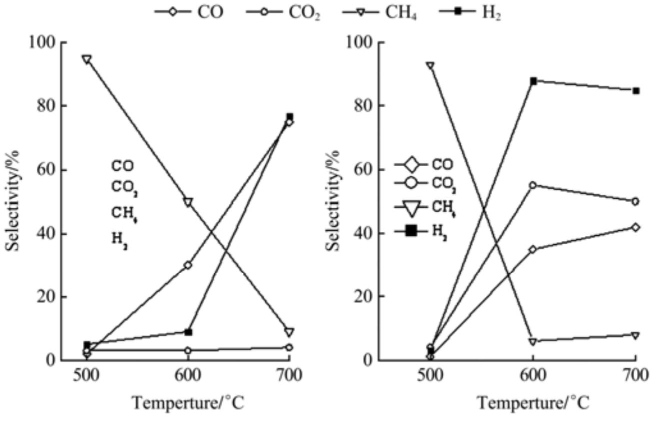
3.1.1 Influence of Ni loading

The results of catalytic SR of acetic acid were given in Figures 2 and 3, with the observation that the maximum H_2 yield was found to be about 52.4% over 30.5% Ni/γ-Al_2O_3 at 600°C. H_2 production was higher in the case of 30.5% Ni/γ-Al_2O_3 catalyst than 16.8% Ni loading, which were produced at the same operating conditions.



a. 16.8% Ni loading b. 30.5% Ni loading

Figure 2 Yields of gas products from SR of acetic acid over catalysts with different Ni loadings



a. 16.8% Ni loading b. 30.5% Ni loading

Figure 3 Selectivity to gas products of SR of acetic acid over catalysts

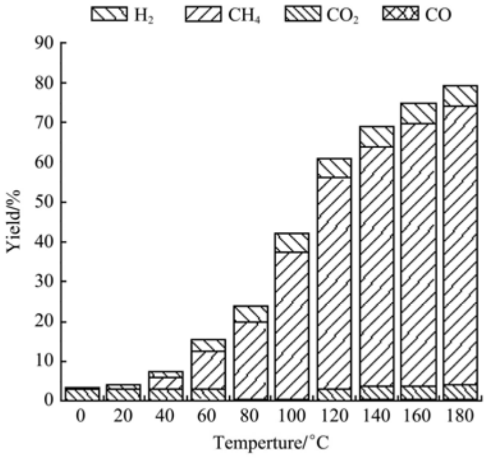
It was revealed that metal content had a significant effect on selectivity in some other literatures[26-28]. After comparison, catalysts with 30.5% Ni loading was more active for acetic acid reforming, besides, the selectivity to hydrogen was also enhanced with the increase of Ni contents, due to the obvious CH_4 decreasing. However, experiments with Ni loading greater than 30.5% were not carried out, we could not speculate that the 30.5% Ni loading was the optimal metal loading for achieving the best catalytic performance.

3.1.2 Influence of reaction temperature

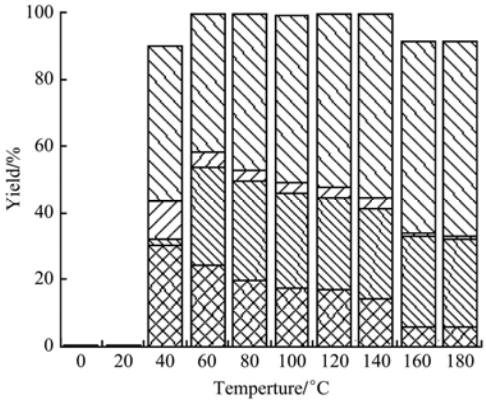
The 30.5% Ni/γ-Al_2O_3 catalyst was tested in temperature range of 500-700°C, each experiment was carried out for 3 h. The experimental results were shown in Figure 3b and Figure 4. It is observed that the conversion of acetic acid increasing with running time, and also observed that reaction temperature had a significant effect on H_2 yield.

As temperature increased from 500°C to 600°C, the increase of CO_2 yield and selectivity and a significant increase of hydrogen yield and selectivity indicated that the SR of acetic acid reaction (Equation (2)) was an endothermic process. As the increase of hydrogen and CO_2, carbon monoxide shift reaction (Equation (7)) occurred hydrogen and CO_2 increasing, while the amount of CO increased. Generally, higher temperature was prone to methanation reaction (Equations (8) and (9)). However, methane yield and selectivity decreased mostly with the increase of temperature. As has been suggested earlier, the conversion of acetic acid to methane was also probably due to thermal decomposition. Methane is an undesirable product for hydrogen production since it leads to reduction in hydrogen yield by competing for the H atoms in the reaction system[29]. The increase of selectivity at lower temperatures can be ascribed to Equation (7), which occurs spontaneously at low temperatures.

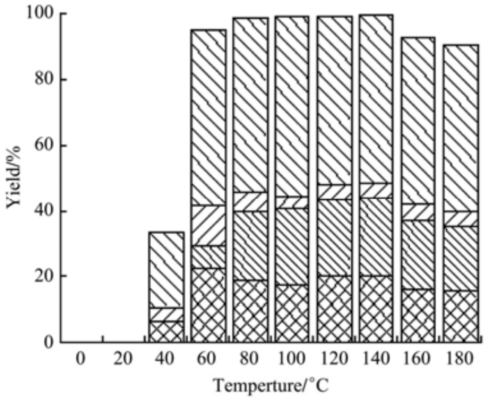
We simulated the influence of reaction temperature from 100°C to 1000°C on the four gas product at S/C ratio of 6:1, and the simulation results are shown in Figure 5. The reactants are acetic acid and H_2O, the composition are likely acetic acid, H_2O, carbon monoxide, carbon dioxide, methane and hydrogen when reaction equilibrium is reached. The studies of thermodynamic simulation using the thermodynamic equilibrium calculations is non-stoichiometric method, which is based on the direct minimization of the Gibbs free energy[30-32] and needs no knowledge of the chemical reactions involved in a system. More details are presented in Reference [8]. The measured results from catalytic SR of acetic acid were basically the same as those simulated results. Increasing reaction temperature was favorable for catalytic SR of acetic acid for hydrogen production, but it was not good when the temperature was higher, which reached the maximum yield around 600°C in this study.



a. 500°C

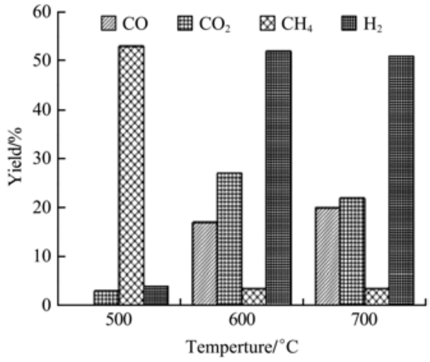


b. 600°C

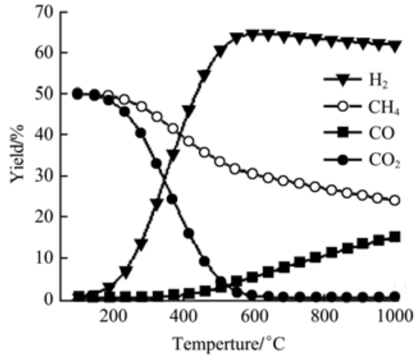


c. 700°C

Figure 4 Yields of gas products from SR of acetic acid at different temperatures with catalyst of 30.5% Ni/γ-Al_2O_3



a. Measured results



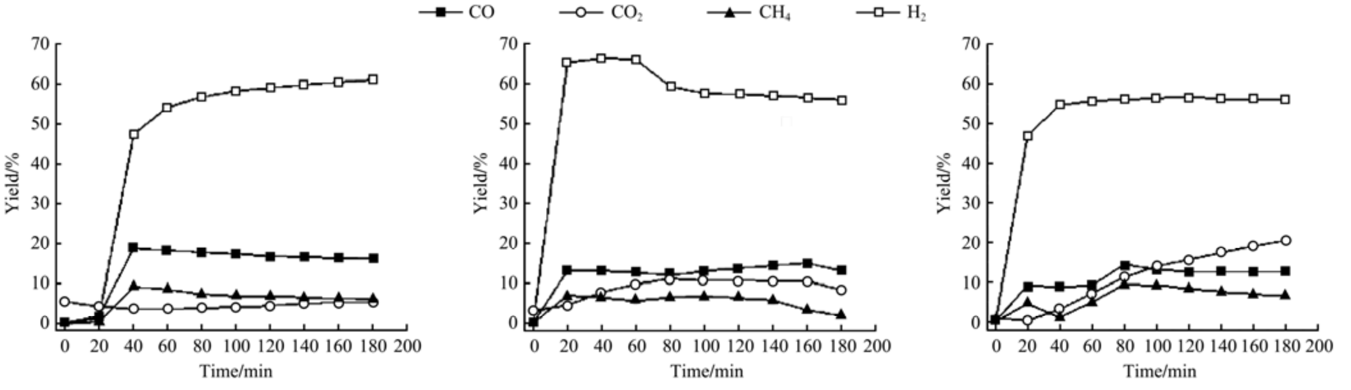
b. Simulated results

Figure 5 The yield of gas products from SR of acetic acid with temperature

3.2 SR of bio-oil over 30.5% Ni/γ-Al_2O_3 catalysts

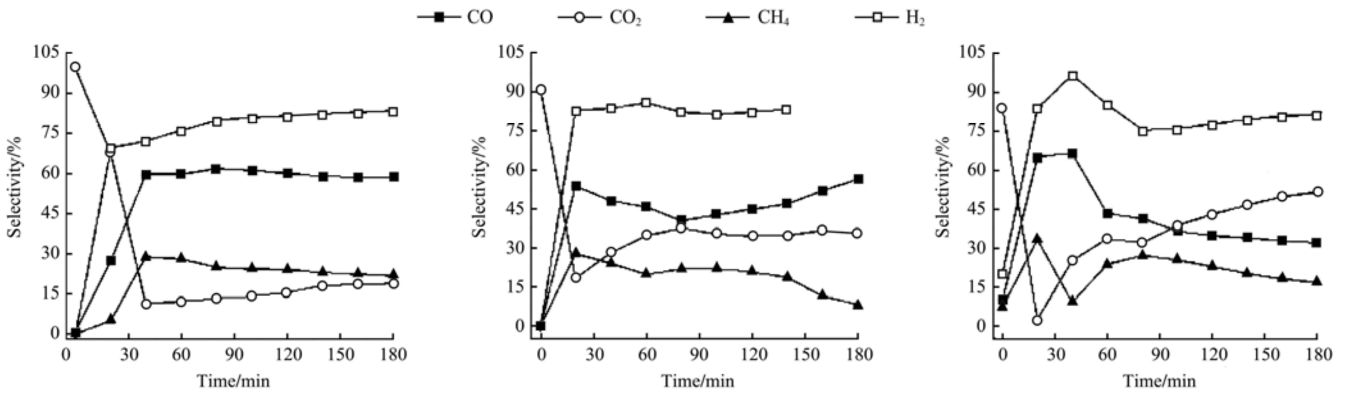
Preliminary experiments of SR of bio-oil over Ni/γ-Al_2O_3 catalysts indicated that higher gaseous yield was obtained with 30.5% Ni content. In order to simplify experiment process, 30.5% Ni/γ-Al_2O_3 catalyst was tested at different temperatures in the process of SR of bio-oil, which was similar to these found in model compounds. Each experiment was carried out for 3 h.

The fluctuations of the products yields and selectivity were observed over time, as shown in Figures 6 and 7. The SR of bio-oil was similar to these found in model compounds under the same conditions. A steady H_2 yield of 65% leveled off after the first 20 min was found at 600°C, so we concluded that 600°C was more favorable temperature for hydrogen production. At the same time, the production of CO_2 also increased with time, whereas, the opposite trend for CH_4 yield was observed. Figure 7 shows that the selectivity to H_2 is between 80% and 90% which is higher than that in SR of acetic acid reaction at each corresponding reforming temperature. CO selectivity is basically around 40%-60%



a. 500℃ b. 600℃ c. 700℃

Figure 6 SR of bio-oil at various temperatures with 30.5% Ni/γ-Al_2O_3 catalysts



a. 500℃ b. 600℃ c. 700℃

Figure 7 Effect of temperature on gaseous selectivity of steam reforming SR of bio-oil and decreases with the temperature increasing. The selectivity of CO_2 varies from 15% to 45%. Overall, H_2 and CO_2 selectivities increase, while CH_4 and CO selectivities decrease with the increase of temperature. The reaction temperature has significant effects on the selectivities of CO and CO_2 and slight effects on the selectivities of H_2 and CH_4.

4 Conclusions

Hydrogen production from catalytic steaming reforming of corn stalk fast pyrolysis bio-oil and acetic acid using Ni/γ-Al_2O_3 catalysts was studied in a laboratory scale fixed bed coupled with the infrared gas analyzer. The effects of Ni loading and reaction temperature on hydrogen production were studied. The highest hydrogen yield of 52.4% was obtained over the 30.5%Ni/γ-Al_2O_3 catalyst at 600°C by catalytic SR of acetic acid. The hydrogen yield was significantly increased when the temperature increased from 500°C to 600°C, whereas hydrogen yield decreased slightly by further increasing the temperature up to 700°C. Catalytic SR of bio-oil with 30.5% Ni/γ-Al_2O_3 catalysts under different temperatures was similar to these found in model compounds. The highest hydrogen yield obtained was 65% at 600°C, and obtained the same hydrogen yield, while the required SR temperature for SR of bio-oil was lower than that of acetic acid.

Acknowledgments

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[References]

[1] Nashawi I S, Malallah A, Al-Bisharah M. Forecasting world crude oil production using multicyclic hubbert model. Energy Fuels, 2010; 24: 1788–800.

[2] Sorrell S, Speirs J, Bentley R, Brandt A, Miller R. Global oil depletion: A review of the evidence. Energy Policy, 2010; 38: 5290–5295.

[3] Nogueira F G E, Assaf P G M, Carvalho H W P,,Assaf E M. Catalytic steam reforming of acetic acid as a model compound of bio-oil. Applied Catalysis B: Environmental, 2014; 160(7): 188–199.

[4] Wang G H. Introduction of new energy. Beijing: Chemical Industry Press, 2006.

[5] Levin D B, Chahine R. Challenges for renewable hydrogen production from biomass. Intl. J Hydrogen Energy, 2010; 35(10): 4962–4969.

[6] Report Code: EP 1708Global hydrogen generation market by merchant & capitive type, distributed & centralized generation, application & technology-trends & forecasts (2011-2016). Markets and Markets; 2011.

[7] Department of Energy of the United States of America. Energy efficiency & renewable energy. Hydrogen production technology, http://www1.eere.energy.gov/hydrogenandfuelscells/production/natural_gas.hltm.

[8] Fu P, Yi W M, Li Z H, Bai X Y, Zhang A D, Li Y M. Investigation on hydrogen production by catalytic steam reforming of maize stalk fast pyolysis bio-oil. Intl. J Hydrogen Energy, 2014; 39(26): 13962–139671.

[9] Wang S R, Cai Q J, Zhang F, Li X B, Zhang L, Luo Z Y. Hydrogen production via catalytic reforming of the bio-oil model compounds: Acetic acid, phenol and hydroxyacetone. Intl. J Hydrogen Energy, 2014; 39(32): 18675–18687.

[10] Ni M, Leunng D, leung M. A review on reforming bio-ethanol for hydrogen production. Intl. J Hydrogen Energy, 2007; 32: 3238–3247.

[11] Bimbela F, Oliva M, Gacia L, Ruiz J, Arauzo J. Hydrogen production by catalytic steam reforming of acetic acid, a model compound of biomass pyrolysis liquids. Journal of Analytical and Applied Pyrolysis, 2007; 79(1): 112–120.

[12] Basagiannis A C, Verykios X E. Reforming reaction of acetic acid on nickel catalysts over a wide temperature range. Applied Catalysis A: General, 2006; 308: 182–193.

[13] Fatsikostas A N, Verykios X E. Reaction network of steam reforming of ethanol over Ni-based catalysts. Journal of Catalysis, 2004; 225:439–452.

[14] Wu C, Liu R H. Carbon deposition behavior in steam reforming of bio-oil model compound for hydrogen production. Intl. J Hydrogen Production, 2010; 35: 7386–7398.

[15] Bimbela F, Oliva M, Gacia L, Ruiz J, Arauzo J. Catalytic steam reforming of model compounds of biomass pyrolysis liquids in fixed bed. Journal of Analytical and Applied Pyrolysis, 2009; 85(1): 204–213.

[16] Trane R, Dahl S, Skjth-Rasmussm M S, Jensen A D. Catalytic steam reforming of bio-oil. Intl. J Hydrogen Energy, 2012; 37(8): 6447−6472.

[17] Perego C, Villa P P. Catalyst preparation methods. Catal Today, 1997; 34: 281−305.

[18] Fatsikostas A N, Kondarides D I, Verykios X E. Production of hydrogen for fuel cells by reformation of biomass-derived ethanol. Catal Today, 2002; 75: 145−155.

[19] Hu X, Lu G X. Investigation of the steam reforming of a series of model compounds derived from bio-oil for hydrogen production. Applied Catalysis B: Environmental, 2009; 88(3-4): 376−385.

[20] Thaicharoensutcharittham S, Meeyoo V, Kitiyanan B, Rangsunvigit P, Rirksomboon T. Hydrogen production by steam reforming of acetic acid over Ni-based catalysts. Catal Today, 2011; 164(1): 257−261.

[21] Pant K K, Mohanty P, Agarwal S, Dalai A K. Steam reforming of acetic acid for hydrogen production over bifunctional Ni–Co catalysts. Catal Today, 2013; 207: 36−43.

[22] Hu X, Lu G X. Acetic acid steam reforming to hydrogen over Co–Ce/Al_2O_3 and Co–La/Al_2O_3 catalysts—the promotion effect of Ce and La addition. Catal Communications, 2010; 12(1): 50−53.

[23] Hu X, Zhang L J, Lu G X. Pruning of the surface species on Ni/Al_2O_3 catalyst to selective production of hydrogen via acetone and acetic acid steam reforming. Applied Catalysis A: Gernal, 2012; 427: 49−57.

[24] Vagia E C, Lemonidou A A. Hydrogen production via steam reforming of bio-oil components over calcium aluminate supported nickel and noble metal catalysts. Applied Catalysis A: Gernal, 2008; 351(1): 111−121.

[25] Li Z K, Hu X, Zhang L J, Lu G X. Renewable hydrogen production by a mild-temperature steam reforming of the model compound acetic acid derived from bio-oil. Journal of Molecular Catalysis A: Chemical, 2012; 355: 123−133.

[26] Garcia L, French R, Czernik S, Chornet E. Catalytic steam reforming of bio-oils for the production of hydrogen: effects of catalyst composition. Applied Catalysis A: Gerneral, 2000; 201: 225−239.

[27] Hou T, Yuan L X, Ye T Q, Gong L, Tu J. Hydrogen production by low-temperature reforming of organic compounds in bio-oil over a CNT-promoting Ni catalyst. Intl. J Hydrogen Energy, 2009; 34 (22): 9095−9107.

[28] Basagiannis A C, Verykios X E. Catalytic steam reforming of acetic acid for hydrogen production. Intl. J Hydrogen Energy, 2007; 32 (15): 3343−3355.

[29] Goyal N, Pant K K, Gupta R. Hydrogen by steam reforming of model bio-oil using structured Ni/γ-Al_2O_3 catalysts. Intl. J Hydrogen Energy, 2013; 38: 921−933.

[30] Hajjaji N, Pons M. Hydrogen production via steam and autothermal reforming of beef tallow: a thermodynamic investigation. Intl. J Hydrogen Energy, 2013; 38(15): 2199−2211.

[31] Cheng C K, Foo S Y, Adesina A A. Thermodynamic analysis of glycerol-steam reforming in the presence of CO_2 or H_2 as carbon gasifying agent. Intl. J Hydrogen Energy, 2012; 37(13): 10101−10110.

[32] Wang J H, Chen H, Tian Y, Yao M F, Li Y D. Thermodynamic analysis of hydrogen production for fuel cells from oxidative steam reforming of methanol. Fuel, 2012; 97: 805−811.