Preparation of Hydrogen through Catalytic Steam Reforming of Bio-oil

WU Ceng (吴 层),　 YAN Yong-jie (颜涌捷),　 LI Ting-chen (李庭琛),　 QI Wei (亓 伟)

(*Department of Energy Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China*)

Abstract: Hydrogen was prepared via catalytic steam reforming of bio-oil which was obtained from fast pyrolysis of biomass in a fluidized bed reactor. Influential factors including temperature, weight hourly space velocity (WHSV) of bio-oil, mass ratio of steam to bio-oil (S/B) as well as catalyst type on hydrogen selectivity and other desirable gas products were investigated. Based on hydrogen in stoichiometric potential and carbon balance in gaseous phase and feed, hydrogen yield and carbon selectivity were examined. The experimental results show that higher temperature favors the hydrogen selectivity by H_2 mole fraction in gaseous products stream and it plays an important role in hydrogen yield and carbon selectivity. Higher hydrogen selectivity and yield, and carbon selectivity were obtained at lower bio-oil WHSV. In catalytic steam reforming system a maximum steam concentration value exists, at which hydrogen selectivity and yield, and carbon selectivity keep constant. Through experiments, preferential operation conditions were obtained as follows: temperature 800~850℃, bio-oil WHSV below 3.0 h^{-1}, and mass ratio of steam to bio-oil 10~12. The performance tests indicate that Ni-based catalysts are optional, especially Ni/α-Al$_2$O$_3$ effective in the steam reforming process.

Key words: fast pyrolysis; bio-oil; hydrogen; steam reforming; Ni-based catalyst; carbon selectivity

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1　INTRODUCTION

Preparation of hydrogen from biomass as raw material has attracted more and more attention in the world. For many years, fossil fuels have played an important role in traditional hydrogen production process. But the depletion of natural fossil fuel reserves, continual price rising and serious environmental problems make people pay more attention focusing on hydrogen production from renewable energy sources. Renewable energy sources are clean and will not run out by reasonable utilization. Because of their consistent long-term availability, renewable energy resources are also inherently more stable in price than fossil fuels[1,2]. Hydrogen production from renewable resources such as biomass can reduce the emissions of SO_2 and NO_x remarkably, it is an environmentally friendly process. Biomass can be used to produce hydrogen-rich gas via different technical pathways, i.e. anaerobic digestion, fermentation, metabolic processing, high-pressure supercritical conversion, gasification and pyrolysis[3]. However, high dispersion distribution and low energy density of biomass lead to a high transportation cost for its utilization. As a result, hydrogen production via gasification of biomass on a large scale will be economically limited.

Bio-oil from fast pyrolysis of biomass represents a uniform feedstock that has much higher energy density than that of biomass and could be transported easily from scattered collection stations to a large scale processing plant. Therefore catalytic steam reforming of bio-oil will be one of the most promising and economically viable method for hydrogen production.

Bio-oil production from biomass involves different pyrolysis processes, such as flash pyrolysis[4], vacuum pyrolysis[5] and microwave pyrolysis[6]. Bio-oil is viscous, corrosive, and relatively unstable in nature, and has lower calorific value because of high oxygen content in composition, therefore its application is limited. Catalytic hydrotreatment and catalytic cracking[7−9] of bio-oil are two main routes that have been intensively investigated in recent years. Hydrogen production from bio-oil provides a new route for utilization of bio-oil.

In resent years hydrogen production via steam reforming of bio-oil has attracted more and more attention. But because of the complicated composition of bio-oil and carbon deposition on catalyst surface in reaction process, currently the studies mainly focus on the steam reforming of model compounds in bio-oil and reforming catalysts. Vagia et al.[10] presented the thermodynamic analysis of hydrogen production via

steam reforming using acetic acid, ethylene glycol and acetone as model compounds. Garcia et al.[11] studied the effects of catalyst composition on catalytic steam reforming of bio-oil, and Rioche et al.[12] investgated the steam reforming of model compounds and fast pyrolysis bio-oil on supported nobel metal catalysts.

In this work, fast pyrolysis of bio-oil is used to produce hydrogen through a catalytic steam reforming process with preferential operation conditions and selected catalysts. The effects of temperature, bio-oil WHSV, steam to bio-oil ratio and catalyst type on mole fractions of product gases, purity of desirable product gases, hydrogen yield and carbon selectivity are investigated.

2 EXPERIMENTAL

2.1 Bio-oil and Catalyst

Bio-oil was produced from a fast fluidized bed reactor and the pyrolysis of sawdust was carried out within the temperature range of 480~500℃ with fluidizing agent N_2. The properties of bio-oil are shown in Table 1.

Table 1　Properties of bio-oil

Density (kg/L, 15℃)	Viscidity (Pa·s, 50℃)	Ultimate analysis (%, wet basis)			
		C	H	O	N and S
1.16	$2.53×10^8$	50.30	6.93	41.84	0.93

Four types of catalyst were tested in the experiment, porcelain chips (blank experiment), dolomite (calcined at the temperature of 900℃ for 5 h), Ni/α-Al_2O_3 and Ni/dolomite.

The catalyst Ni/α-Al_2O_3 was prepared by impregnation method. Firstly $Ni(NO_3)_2·6H_2O$ was dissolved in deionized water and the concentration of $Ni(NO_3)_2$ solution was adjusted at 0.5 mol/L. Then α-Al_2O_3 powder (particle sizes in 355~600 μm) was mixed with the excessive $Ni(NO_3)_2$ solution agitating for 6 h. Through filtration the solid impregnated with nitrate was then dried at 80℃ for 48 h and calcined at 800℃ for 5 h (heating rate was kept at 10℃/min before 300℃). The powder was then pressed, crushed and sieved to a particle size range of 2~3 mm. The preparation method for catalyst Ni/dolomite is the same as that of Ni/α-Al_2O_3.

2.2 Flowsheet and Operation

The experimental installation is shown in Fig.1 as the flowsheet for steam reforming process. Bio-oil is kept in a constant temperature bath at the temperature of 50℃ for the convenience of feeding. Feeding rates of bio-oil and water are controlled by two metering pumps. Reaction products are condensed and the condensate is collected in a liquid receiver. The non-condensed components of product gases are sampled and their contents are determined by GC analysis.

1. Nitrogen cylinder
2. Gas meter
3. Water
4. Metering pump I
5. Steam generator
6. Reactor
7. Heater
8. Thermocouple
9. Temperature controller
10. Metering pump II
11. Bio-oil container
12. Water bath
13. Condenser
14. Liquid receiver
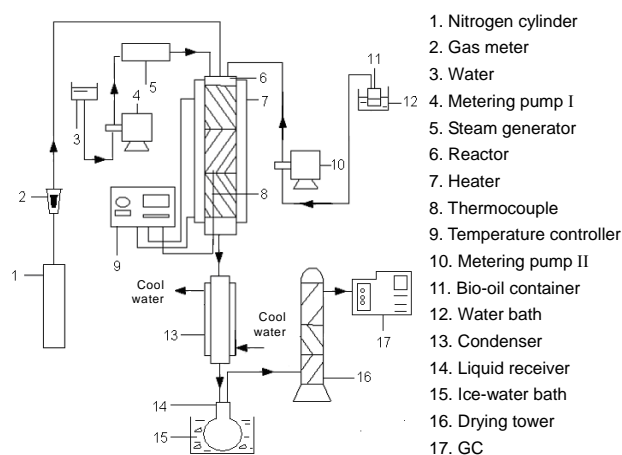15. Ice-water bath
16. Drying tower
17. GC

Fig.1 Schematic diagram of experimental apparatus

Nitrogen from the cylinder is regulated at the flow rate of 0.3 L/min while the reactor and steam generator are preheated. Both of bio-oil and steam are fed from the top of reactor when temperature reaches the setting value. Product gases are sampled for quantitative analysis with GC. To reduce the influence of accidental error on experimental result, three groups of parallel experiment are carried out. The experimental data can be regarded as effective ones when the relative error between them is lower than 3%.
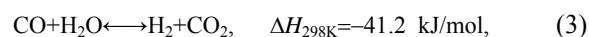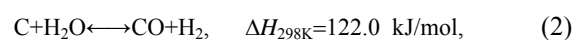
2.3 Chemical Reaction and Data Analysis

As the components of bio-oil are numerous and complex, $C_nH_mO_z$ is used to represent their basic chemical formula. Given that the reaction has reached to completion, the steam reforming of bio-oil can be expressed in the following reaction:

$$C_nH_mO_z+(2n-z)H_2O→(2n+m/2-z)H_2+nCO_2. \quad (1)$$
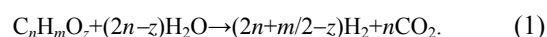
But actually bio-oil components are in general thermally unstable at the typical temperatures of the reformer[13–15]. So a mixture of gases (H_2, CO, CO_2, CH_4, unsaturated hydrocarbon,···) and coke will form as primary products because of thermal decomposition of bio-oil. Then the primary products go through catalyst bed for catalytic steam reforming process. Water–gas shift (WGS) reaction will take place on catalyst bed and the hydrogen-rich syngas can be obtained.

The main reactions involved on the catalyst bed are listed as follows:

$$C+H_2O⟷CO+H_2, \quad ΔH_{298K}=122.0 \text{ kJ/mol}, \quad (2)$$

$$CO+H_2O⟷H_2+CO_2, \quad ΔH_{298K}=-41.2 \text{ kJ/mol}, \quad (3)$$

$$CH_4+2H_2O⟷4H_2+CO_2, \quad ΔH_{298K}=164.9 \text{ kJ/mol}. \quad (4)$$

The WGS reaction for CO is exothermic and can be carried out at lower temperature. But WGS reaction for CH_4 is much more difficult than that of CO. For endothermic reaction system, high temperature and the presence of catalyst are necessary to achieve the efficient conversion of CH_4. Therefore, the total content of H_2 and CO can be regarded as the desirable product gases purity (y), which is defined as:

$$y = \frac{\text{Moles of } H_2, CO \text{ obtained}}{\text{Moles of } H_2, CO, CH_4 \text{ obtained}} \times 100\% . \quad (5)$$

According to the elemental analysis in Table 1, molecular formula of bio-oil can be represented by $CH_{1.66}O_{0.63}$ (wet basis). Bio-oil contains 33.0%(ω) water, and $CH_{0.78}O_{0.19}$ can be used to represent the bio-oil molecular formula in dry basis. The theoretical maximum hydrogen yield (100%) can be obtained when steam reforming of bio-oil achieves completion and produces hydrogen and carbon dioxide only, which can be expressed as:

$$CH_{0.78}O_{0.19} + 1.81H_2O \rightarrow 2.20H_2 + CO_2. \quad (6)$$
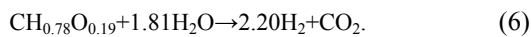
The mole ratio of H_2 obtained to H_2 in stoichiometric potential is defined as hydrogen yield one (Y_1), which can be expressed as follows:

$$Y_1(\%) = \frac{\text{Moles of } H_2 \text{ obtained}}{\text{Moles of } H_2 \text{ in stoichiometric potential}} \times 100\% . \quad (7)$$

The mole ratio of H_2 and CO obtained to H_2 in stoichiometric potential is defined as hydrogen yield two (Y_2), it can be expressed as follows:

$$Y_2(\%) = \frac{\text{Moles of } H_2 \text{ and CO obtained}}{\text{Moles of } H_2 \text{ in stoichiometric potential}} \times 100\% . \quad (8)$$

In the experiment, another important parameter that should be investigated is the utilization efficiency of bio-oil. Carbon element takes up half of the bio-oil (by weight in wet basis) and the increase of carbon element in product gases means the yield increase of product gases. We define carbon selectivity S_C as follows:

$$S_C(\%) = \frac{\text{Moles of CO, } CH_4, CO_2 \text{ obtained}}{\text{Moles of carbon in feed}} \times 100\% . \quad (9)$$

3 RESULTS AND DISCUSSION

3.1 Effect of Temperature

The pyrolysis reaction proceeded in the presence of dolomite as catalyst under the conditions of bio-oil WHSV 1.2 h^{-1}, and mass ratio of steam to bio-oil 15, and steam reforming of bio-oil was carried out in the temperature range of 700~850 ℃.

Figure 2 shows that the increase of reaction temperature favors the hydrogen selectivity by H_2 mole fraction increasing from 50.1% to 62.1%. On the contrary, CO shows a downtrend from 16.3% to 3.6%. CH_4 decreases slightly from 7.0% to 5.4% and CO_2 increases from 26.6% to 28.9%. The purity of desirable product gases as defined before shows an uptrend from 700 to 800 ℃, and the purity 93% is achieved at nearly 800 ℃. In consideration of H_2 selectivity and purity, 800 ℃ is regarded as preferential reaction temperature.
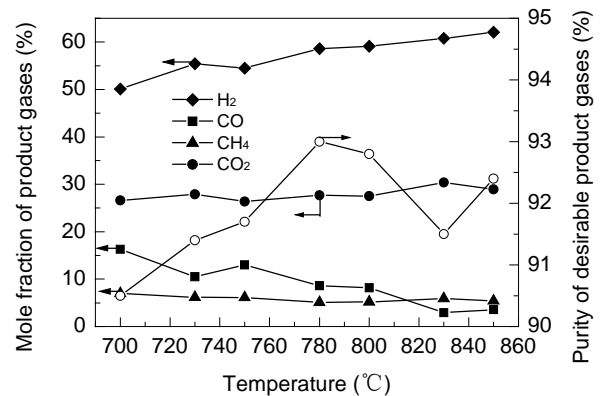

Fig.2 Effect of temperature on product distribution

Figure 3 indicates that temperature plays an important role in hydrogen yield and carbon selectivity. The hydrogen yield and carbon selectivity increase dramatically within the temperature range. The maximum hydrogen Y_1 57.0%, Y_2 60.3% and carbon selectivity 76.6% are obtained at 850 ℃. To enhance the utilization efficiency of bio-oil and hydrogen yield, the reaction should be carried out at relatively higher temperature. But in consideration of the reactor load and energy consumption, 800~850 ℃ is chosen as the preferential reaction temperature range.
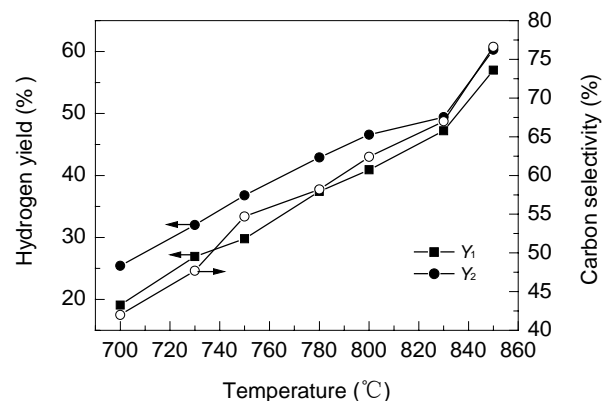

Fig.3 Effect of temperature on hydrogen yield and carbon selectivity

Increase of temperature favors the carbon element shift from bio-oil to gaseous phase in the forms of CO,

CH_4 and CO_2. The carbon element loss in steam reforming process is mainly in the form of coke, as tar and the components in bio-oil reacted incompletely. At higher temperature, the carbon element in bio-oil could be converted into gaseous phase efficiently, accordingly the hydrogen yield increases.

3.2　Effect of Weight Hourly Space Velocity (WHSV)

The pyrolysis reaction proceeded in the presence of dolomite as catalyst under the conditions of temperature 800℃ and mass ratio of steam to bio-oil 15, and steam reforming of bio-oil was carried out in WHSV range of $0.7\sim8.3$ h^{-1}.

Figure 4 shows that H_2 mole fraction keeps decreasing from 61.0% to 40.9% within the WHSV range of $0.7\sim8.3$ h^{-1}. However, CO fraction shows an obvious uptrend, increasing from 4.3% to 27.2% and CH_4 fraction increases from 4.9% to 13.4%, but CO_2 mole fraction decreases from 29.8% to 18.5% in the whole range. As to the purity of desirable product gases, it has a trend parallel to that of H_2, from 93.0% to 83.6%.
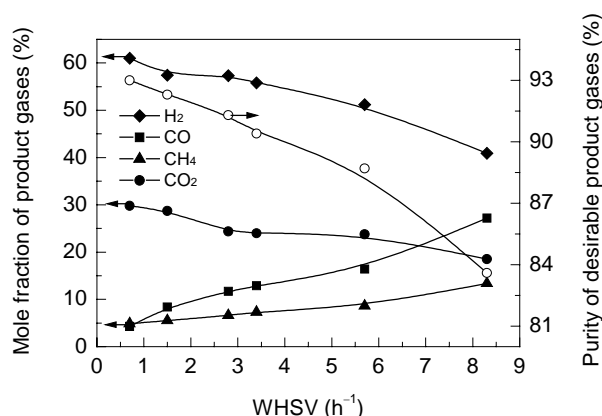

Fig.4 Effect of WHSV on product distribution

The results of WHSV effect on hydrogen yield and carbon selectivity are given in Fig.5. The higher the WHSV is, the lower the hydrogen yield and carbon selectivity are. The maximum hydrogen Y_1 60.4%, Y_2 65.2% and carbon selectivity 86.4% are obtained at 0.7 h^{-1} of WHSV. Within the range $0.7\sim2.8$ h^{-1}, hydrogen yield and carbon selectivity decrease rapidly and then keep at a lower level when it is more than 3.0 h^{-1}.

Based on the proposed two-step process theory in the section 2.3, with increasing of WHSV, concentration of primary products increases on one hand. On the other hand, the residence time of primary products on the catalyst bed decreases. So three main WGS reactions on the bed as mentioned before are inhibited.

For desirable product gases, it is not economically feasible when the purity less than 90%. Therefore, in order to obtain higher mole fraction of H_2 and desirable product purity, and keep the hydrogen yield and carbon selectivity at higher level in the meantime, WHSV should be kept below 3.0 h^{-1}.
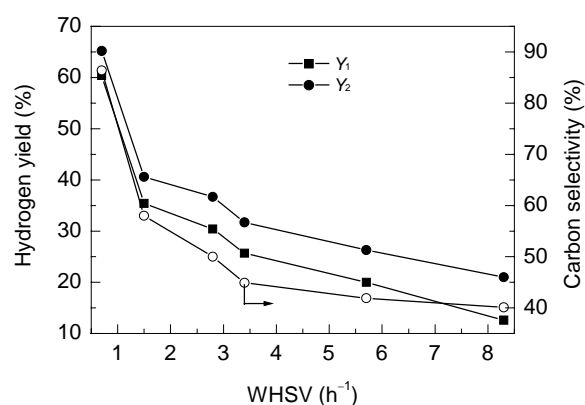

Fig.5 Effect of WHSV on hydrogen yield and carbon selectivity

3.3　Effect of Mass Ratio of Steam to Bio-oil (S/B)

The pyrolysis reaction proceeded in the presence of dolomite as catalyst under the conditions of temperature 800℃ and bio-oil WHSV 1.2 h^{-1}, and steam reforming of bio-oil was carried out in S/B ration range of $1\sim20$.

As shown in Fig.6, the effect of mass ratio of steam to bio-oil on production of H_2, CO, CH_4, and CO_2, and desirable product gases purity is significant. When S/B is below 10, H_2 mole fraction increases from 43.0% to 58.2% with the increase of S/B. CO fraction firstly shows an obvious downtrend in the S/B range $1\sim5$ and then increases slightly. CO_2 fraction shows a contrary trend with that of CO. CH_4 fraction decreases from 15.1% to 5.9% and the purity of desirable product gases increases from 80.4% to 91.9% in the S/B range $1\sim10$. The mole fraction of each component is almost kept constant when S/B is more than 10.
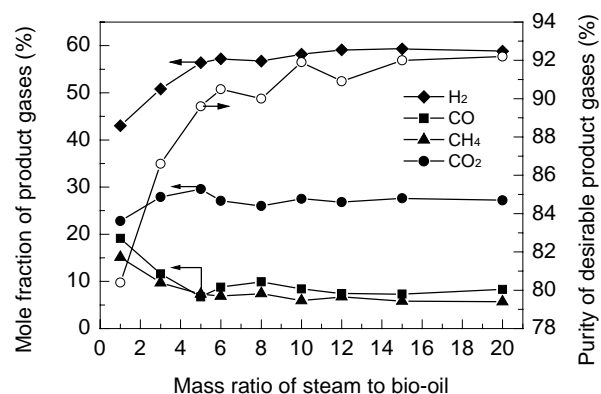

Fig.6 Effect of mass ratio of steam to bio-oil on

As to the hydrogen yield and carbon selectivity shown in Fig.7, the ratio of steam to bio-oil is another critical influential parameter. In the S/B range of $1\sim12$,

hydrogen yield and carbon selectivity show an obvious uptrend and the maximum Y_1 40.9%, Y_2 46% and carbon selectivity 62.4% are obtained at S/B 12. When S/B is more than 12, each parameter is almost kept constant.
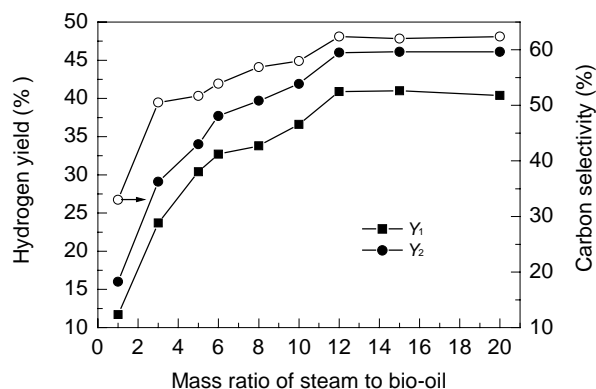

Fig.7 Effect of mass ratio of steam to bio-oil on hydrogen yield and carbon selectivity

Based on the results above, in steam reforming system an optimal steam value exists, at which mole fraction of product gases, hydrogen yield and carbon selectivity keep constant. In the experiments, S/B 10~12 is the optimal value.

3.4 Effect of Catalyst Type

The pyrolysis reaction proceeded under the conditions of temperature 800 ℃, mass ratio of steam to bio-oil 12 and bio-oil WHSV 1.2 h^{-1}. Four types of catalyst are selected to use in the experiments, porcelain chips (Catalyst 1, blank experiment), dolomite (Catalyst 2) calcined at 900 ℃ for 5 h, Ni/dolomite (Catalyst 3), and Ni/α-Al$_2$O$_3$ (Catalyst 4).

As shown in Fig.8, for catalyst dolomite (Catalyst 2), H$_2$ mole fraction is 57.5%, which is 14.0% more than that of blank experiment. CO and CH$_4$ fractions are 8.9% and 5.7%, respectively. But for Ni-based catalyst Ni/dolomite (Catalyst 3) and Ni/α-Al$_2$O$_3$ (Catalyst 4), H$_2$ fractions reach 61.0% and 61.9%, respectively, which

are 17.5% and 18.4% more than that of blank experiment. CO fraction for Catalyst 3 is 5.6% and for Catalyst 4 5.5%. CH$_4$ fraction for Catalyst 3 is 5.4% and for Catalyst 4 4.0%. For Catalysts 2, 3 and 4, CO$_2$ mole fraction is almost at the same level. The desirable product gases purity values in four groups of experiments are 87.1%, 92.1%, 92.5% and 94.4%, respectively.
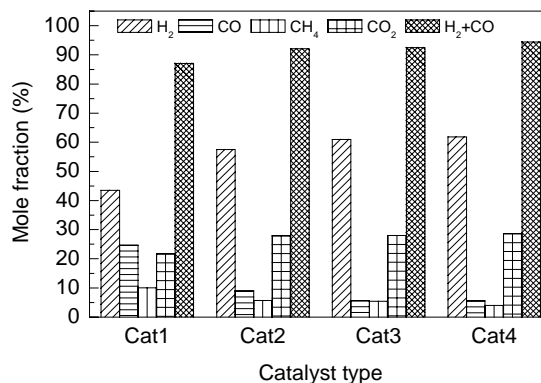

Fig.8 Effect of catalyst type on product distribution

The effect of catalyst type on hydrogen yield and carbon selectivity is shown in Figs.9 and 10. Catalysts 2, 3 and 4 are efficiently catalytic in steam reforming process in comparison with blank experiment. Higher catalytic effect is achieved by Ni-based catalysts, Catalysts 3 and 4. Hydrogen yields Y_1 45.4%, Y_2 49.6% and carbon selectivity 64.0% are obtained by Catalyst 3. Y_1 47.7%, Y_2 51.9% and carbon selectivity 64.6% are obtained by Catalyst 4.

From the above results, we can conclude that the water–gas shift reaction of C, CO and CH$_4$ can be carried out efficiently on Ni-based catalyst. In the experiments, the maximum H$_2$ mole fraction 61.9%, desirable product gases purity 94.4%, hydrogen yields Y_1 47.7%, Y_2 51.9% and carbon selectivity 64.6% are obtained by catalyst Ni/α-Al$_2$O$_3$.
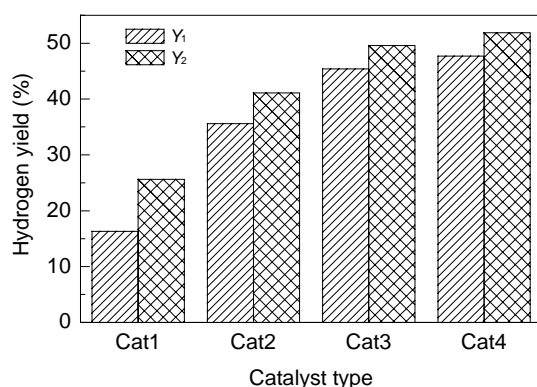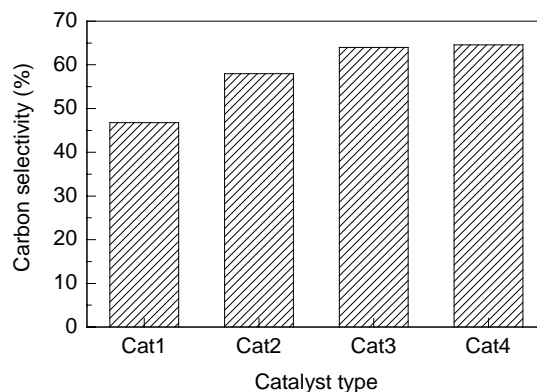

Fig.9 Effect of catalyst type on hydrogen yield

Fig.10 Effect of catalyst type on carbon selectivity

4 CONCLUSIONS

Catalytic steam reforming of fast pyrolysis of bio-oil is a potentially viable route for hydrogen production. In this experimental work, elementary technological conditions were studied in order to gain the maximum hydrogen selectivity and desirable product gases purity as well as hydrogen yield and carbon selectivity. Some conclusions can be drawn as follows:

(1) Higher temperature favors the hydrogen selectivity by H_2 mole fraction in gaseous products stream and influences hydrogen yield and carbon selectivity strongly.

(2) Higher hydrogen selectivity and yield, and carbon selectivity can be obtained at lower bio-oil weight hourly space velocity (WHSV).

(3) The mass ratio of steam to bio-oil has an optimal value, and increasing the ratio positively affects hydrogen selectivity and yield, and carbon selectivity before it reaches this value.

(4) Through experiments, preferential operation conditions have been set up as follows: temperature 800~850 ℃, bio-oil WHSV below 3.0 h^{-1}, and ratio of steam to bio-oil 10~12. The experimental results indicate that Ni-based catalysts are optional, especially Ni/α-Al_2O_3 is effective in steam reforming process.

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