

## Bio-Oil Upgrading Over Bi-Functional Catalyst in CO/H<sub>2</sub>O System

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The liquid phase upgrading of a model bio-oil was studied over a series of supported Ni catalysts in the CO/H<sub>2</sub>O system. 6 % Ni/B206 catalyst showed the highest activity for deoxygenation, the oxygen content of the model oil decreasing from an initial value of 47.74 wt % to 3.76 wt % after upgrading. In addition, the reason for catalyst deactivation was investigated. The fresh and deactivation catalysts were analyzed by X-ray diffraction, Brunauer-Emmett-Teller, thermogravimetric analysis and scanning electron microscopy, which showed that the carbon deposition is the main reason for catalyst deactivation.

**Key Words:** Bio-oil, Model, Deoxygenation, Upgrading, Catalyst, Carbon monoxide.

### INTRODUCTION

With depletion of fossil fuels and environmental protection awareness, biomass energy has drawn great attention in recent years<sup>1-4</sup>. Biomass has a lot of merits, *i.e.*, regeneration, CO<sub>2</sub> zero emission, cleansing, *etc.* However, as biomass contains high moisture and has low density, it is difficult to transport, store and use without any pretreatment. Therefore, some thermal conversion methods such as pyrolysis and gasification, to produce fuel products, are more preferable. In particular, the pyrolysis process in which solid, liquid and gaseous products are obtained from biomass as a result of heating under non-oxidizing conditions has been widely applied to a number of biomass species<sup>5-11</sup>. The pyrolysis technology was developed quickly. However, the liquid products (called bio-oil), which contain high content of oxygen, are of low calorific value and of poor thermal stability. This disadvantage becomes a problem restricting its extensive application and replacement the fossil fuels. Deficiency of hydrogen and high content of oxygen are two main factors that cause low quality of the bio-oil<sup>12</sup>. Upgrading the liquid products from biomass pyrolysis thus becomes necessary in solving this problem. The present research on upgrading<sup>13-18</sup> focuses on the technological route, *i.e.*, catalytic hydrogenation and catalytic cracking.

Catalytic hydrogenation is a process in which bio-oil is hydro-treated under pressure (10-20 MPa) in the hydrogen ambience. Catalytic thermal cracking is, on the other hand, a process in which bio-oil is thermally treated at atmospheric pressure without hydrogen. Compared with catalytic hydro-

genation, its disadvantages are low yield, easy coking, which lead to a shorter life of catalyst although catalytic thermal cracking proceeds at an atmospheric pressure. In the catalytic hydrogenation process, hydrogen combines with oxygen to form water, increasing the water content in the bio-oil (crude bio-oil contains 15-30 wt % water), which inhibits the hydrogenation reaction proceeding. So the hydrogenation reaction proceeds at a higher temperature (350-500 °C) and higher pressure (10-20 MPa).

In this paper, a new method of upgrading bio-oil is proposed. The method is a process in which bio-oil is treated under pressure (2-6 MPa) in the carbon monoxide ambience. Carbon monoxide and water make up a new CO/H<sub>2</sub>O system in which CO reacts with water to produce hydrogen and hydrogen combines with oxygen to produce water. Compared with direct catalytic hydrogenation, its advantage is the use of water in the crude bio-oil. The whole process doesn't increase the content of water in the bio-oil, which favour the removal of oxygen. In the CO/H<sub>2</sub>O system, catalyst must have two functions. One is favour to the water-gas shift reaction. The other is favour to the hydrogenation reaction. Therefore, in this paper a series of bi-functional catalysts were prepared and applied in the upgrading method of CO/H<sub>2</sub>O system.

### EXPERIMENTAL

**Preparation of catalyst:** The B206 shift catalyst, which was produced by Sinopec Nanjing Catalyst Plant, was crushed and sieved to a certain size, weighing a certain amount of B206

shift catalyst and placing in a beaker. Nickel nitrate solution was dropped into the B206 shift catalyst, stirring on a magnetic stirrer at 40 °C for 12 h and then drying in the oven, finally, calcined at 500 °C for 5 h in the furnace.

According to GC-MS analyzing, bio-oil is made up of more than 200 compounds. A lot of researchers chosen a single-compound as bio-oil model to examine the activity of catalyst, however, a single-compound model have different physical and chemical properties with bio-oil, which led to decrease the catalyst activity on the bio-oil upgrading. In this paper, a mixture of several typical model compounds was chosen as bio-oil model, including acid, glycol, propionaldehyde, acetone, ethyl acetate, *m*-cresol, furfural, guaiacol, ethanol and sucrose, which were reagent grade purity. The molecular formula of this model compound is similar with bio-oil. The composition of bio-oil model was listed in Table-1. The measured pH was 2.5. This composition was chosen to reflect the composition of typical pyrolysis oils with respect to the main compound types and their concentrations.

TABLE-1  
COMPOSITION OF BIO-OIL MODEL

Materials	Weight (g)	Materials	Weight (g)
Acid	80	Glycol	80
Propionaldehyde	80	Furfural	80
Acetone	80	Ethyl acetate	80
<i>m</i> -Cresol	80	Guaiacol	20
Ethanol	60	De-ionized water	340

**Bio-oil upgrading:** Upgrading experiments were carried out in a mechanically stirred 300 mL stainless steel autoclave, which was produced by Dalian Tong Chan High-pressure Reactors Manufacture Co., Ltd. The experimental apparatus was shown in Fig. 1. Experiment includes two parts: (a) the first step is a bi-functional catalyst reduction process, in which the catalyst was deoxygenated under pressure (6 Mpa), temperature (350 °C) in the hydrogen ambience; (b) the other step is a bio-oil model upgrading process, in which the bio-oil model is upgraded in the carbon monoxide ambience. The upgrading process involves two reactions, which are water-gas shift reaction and hydrogenation reaction. In the end, the temperature of autoclave is dropped to room temperature. Once the reactor reached room temperature, a gas sample was taken for analysis, after which the oil, aqueous and solid phases were removed and separated by filtration and centrifuging. The solid product was extracted twice with tetrahydrofuran to yield additional oil. To calculate the amount of solid formed, the weight of catalyst used was subtracted from the weight of the dry solid.

**Product analysis:** Agilent 6820 gas chromatogram equipped with Unibeads C 80/100 column was used for analysis of gaseous products. Elemental analysis was performed on the separated oil phases of the reacted bio-oil using a BCH-1 analyzer, which was produced by Jiangsu Jiangfen Electro-analytical Instrument Co., Ltd. GC/MS analysis of the oil product was performed using a PE Clarus 500 GC/MS with a HP-5 MS capillary column.

**Data analysis:** High quality bio-oil was the desirable product in upgrading bio-oil. The purpose of this work is to

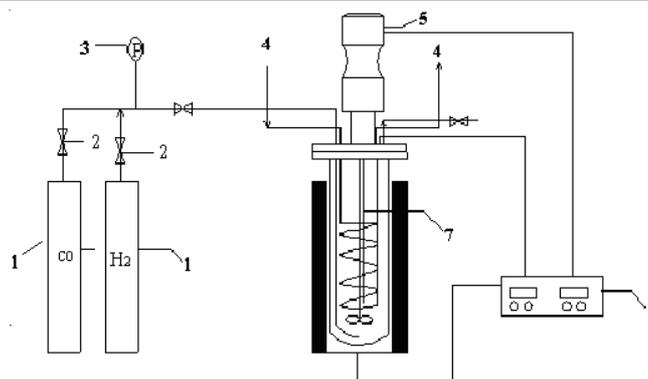


Fig. 1. Schematic diagram of experimental apparatus. 1. Cylinder; 2. Valve; 3. Gauge; 4. Condenser pipe; 5. Electric motor; 6. Control box; 7. Thermocouple

develop catalysts and upgrade the bio-oil quality in an autoclave reactor under certain operation conditions. The equations used in this paper can be shown as follows:

Deoxygenation rate

$$= \frac{\text{Oxygen conten in bio - oil model} - \text{Oxygen conten in the product}}{\text{Oxygen conten in bio - oil model}}$$

$$Y_{\text{oil}} = \frac{\text{Weight of oil phase product}}{\text{Weight of bio - oil model}} \times 100$$

$$Y_{\text{gas}} = \frac{\text{Increase of weight in gaseous phase}}{\text{Weight of bio - oil model}} \times 100$$

$$Y_{\text{Coke}} = \frac{\text{Weight of THF insoluble} - \text{Weight of catalyst}}{\text{Weight of bio - oil model}} \times 100$$

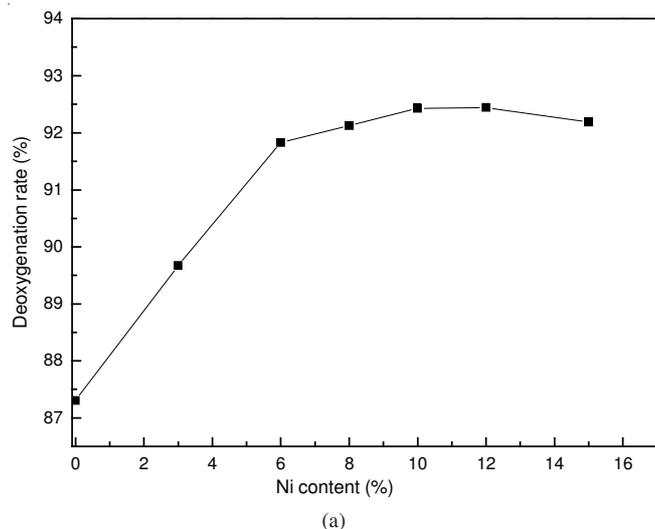
$$\frac{W_{\text{cat}}}{W_{\text{model of bio-oil}}} = \frac{\text{Weight of catalyst}}{\text{Weight of bio - oil model}}$$

## RESULTS AND DISCUSSION

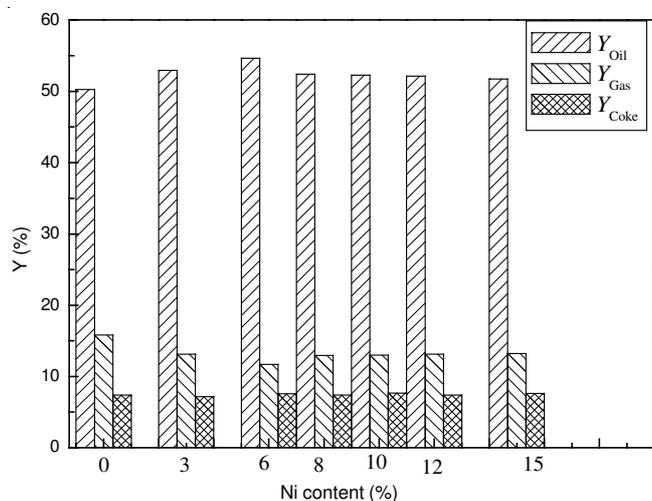
**Screening of supported Ni catalysts:** Upgrading experiments were carried out at pressure (6.0 Mpa), temperature (350 °C), speed (500 r/min), reaction time (2 h),  $W_{\text{cat}}/W_{\text{model of bio-oil}} = 1/10$ , solvent (tetralin, 50 mL) and model of bio-oil (50 mL) in a autoclave. In general, the reaction products comprised four distinct phases *i.e.*, gas, oil, aqueous layer and solid.

The gas, oil and coke yield and deoxygenation rate resulting from treatment of the model bio-oil with the different supported nickel catalysts is shown in Fig. 2.

The results shown in Fig. 2(a) indicated that deoxygenation rate increased with the increase of Ni content at first and then reached a plateau when the Ni content was more then 6 %. That is to say, deoxygenation rate achieved a maximum. As shown in Fig. 2(b), the coke yield was fairly constant for the different catalysts. The oil yield increased with the increase of Ni content at first and then decreased when the Ni content was more then 6 %. The gas yield had an opposite direction of the oil yield. The gas yield decreased with the increase of Ni content at first and then increased slowly when the Ni content was more then 6 %. The reason could be due to the low deoxygenation efficiency caused by the low Ni content. The hydrogenation reaction was limited under a low Ni content.



(a)



(b)

Fig. 2. Gas, oil and solid yields and deoxygenation rate from treatment of model bio-oil with Ni catalysts (reaction time = 2 h)

The higher Ni content had a favour on hydrogenation reaction. On the contrary, with the Ni content increasing, the content of B206 shift catalyst in the bi-functional catalyst decreased, which didn't favour the water-gas shift reaction and the synergic action was restricted. 6 % Ni in the catalyst showed the highest activity for deoxygenation in the CO/H<sub>2</sub>O system, the oxygen content of the bio-oil model decreasing from an initial value of 47.74-3.76 % after upgrading.

**XRD analysis of catalyst:** Its XRD spectra was obtained through diffractive analysis on D/max-2500 X-ray diffraction instrument, equipped with graphite monochromator and with CuK as ray source, operated under the conditions as follows: tunnel voltage 40 kV, current 80 mA and scanning scope 2θ = 10-80°.

The XRD analyses of fresh catalyst and used catalyst were shown in Fig. 3. From the results shown in Fig. 3, diffraction peak is sharp, which indicated that the crystallization of the fresh and used catalyst were in a good condition. The fresh catalyst and the used catalyst have the similar characteristic structures, which reveal that the skeleton structure of catalyst does not change.

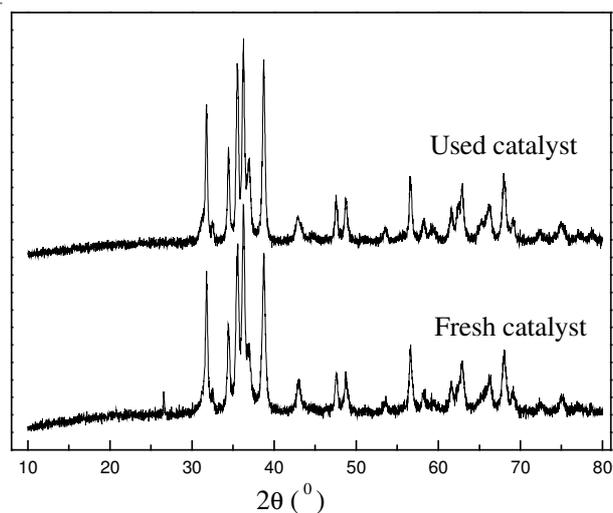


Fig. 3. XRD spectra of fresh and used catalysts

**BET analysis of catalyst:** Specific surface area of the fresh catalyst and used catalyst were measured with the instrument ASAP2420 through nitrogen adsorption.

The BET results indicated that BET surface area and average pore size of fresh catalyst was 44.31 m<sup>2</sup>/g and 12.04 nm. Compared to the fresh catalyst, the BET surface area and average pore diameter of used catalyst was decreased to 32.96 m<sup>2</sup>/g and 11.20 nm. This may be due to carbon deposition on the catalyst surface, which is a main reason for the catalyst deactivation.

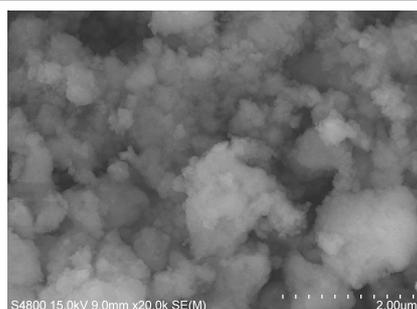
**TGA characterization of catalyst:** Thermal gravimetric analysis was carried out to quantify the carbon deposition content of reacted catalysts. The reacted catalyst was first ground to a powder and a 30 mg sample was placed in the analyzer (NETZSCH, STA409PC) and the sample was initially heated to 100 °C under argon to outgas water. Then, a temperature ramp (10 °C/min from 100-1000 °C) was applied under the atmosphere. A fresh catalyst sample was run under the same conditions as the blank test to revise the weight loss of reacted catalysts.

The TGA results showed that the carbon content of the fresh catalyst was only 0.56 %, but the used catalyst was up to 2.45 %. This could be due to carbon deposition on the surface of catalyst. The results indicated that for bio-oil upgrading in the CO/H<sub>2</sub>O system, carbon deposition is a main reason of catalyst deactivation. This result was the same with Wu and Liu<sup>19</sup> results.

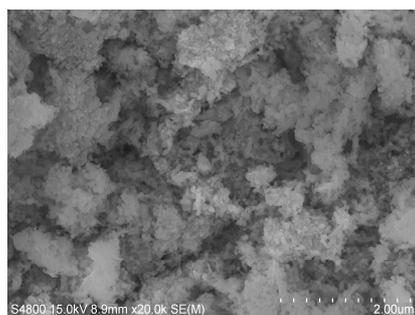
**SEM analysis of catalyst:** The scanning electron microscope (SEM) analyses were shown in Fig. 4. From the results shown in Fig. 4, the SEM image of the fresh catalyst didn't find carbon fiber on the catalyst surface, while the SEM image of used catalyst had some carbon grains, which is the same result of TGA analysis. That is to say, carbon deposition on the surface of catalyst is the main reason for catalyst deactivation. This result in agreement with the BET and TGA analysis.

## Conclusion

There were two reactions in the upgrading method of CO/H<sub>2</sub>O system. One is the water-gas shift reaction and the other is the hydrogenation reaction. The two reactions had a synergic action. 6 % Ni in the catalyst showed the highest activity for deoxygenation in the CO/H<sub>2</sub>O system, the oxygen content of



(a) Fresh catalyst



(b) Used catalyst

Fig. 4. SEM images of fresh and used catalysts: (a) Fresh catalyst, (b) used catalyst

the bio-oil model decreasing from an initial value of 47.74-3.76 % after upgrading. The results of BET, TGA, XRD and SEM analyses showed that carbon deposition is the main reason for catalyst deactivation.

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