

## Bio-Oil Model Compounds Upgrading Under CO Atmosphere

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The bio-oil model upgrading was studied over a series of catalysts in the CO/H<sub>2</sub>O system. The impregnation method was superior to the dry mix method. 6 % of Ni impregnating in B206 catalyst is the optimum bi-functional catalyst. The optimum catalyst showed the highest activity for deoxygenation in the CO/H<sub>2</sub>O system, the deoxygenation rate was up to 92 % and the dehydration rate was 89 % in a certain conditions after upgrading.

**Keywords:** Bio-oil, Model, Deoxygenation, Upgrading, Bi-functional catalyst.

### INTRODUCTION

In recent years, biomass energy as a kind of clean energy has attracted great attention in the world. Biomass can be gasified easily to produce syngas or fuel gas<sup>1,2</sup>. Through hydrolysis and fermentation technologies, biomass can be converted to fuel ethanol<sup>3-5</sup>. Through pyrolysis technologies<sup>6,7</sup>, biomass can be converted to bio-oil. The pyrolysis technologies include ash pyrolysis<sup>8</sup>, microwave pyrolysis<sup>9</sup>, vacuum pyrolysis<sup>10</sup>, vortex pyrolysis<sup>11</sup> and rotating cone pyrolysis<sup>12</sup>. In recent years, 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. Therefore, how to use the bio-oil properly and effectively has attracted researchers' great attention in the world. Bio-oil/diesel emulsion for engine fuel<sup>13,14</sup>, bio-oil separation for valuable chemicals<sup>15-17</sup>, bio-oil gasification for syngas<sup>18</sup>, bio-oil steam reforming for hydrogen production<sup>19,20</sup> and bio-oil upgrading by catalytic cracking<sup>21</sup>, hydro-treatment<sup>22</sup> and esterification<sup>23</sup>, are the main technological routes that researchers studied in recent years.

Deficiency of hydrogen and high content of oxygen are two main factors that cause low quality of the bio-oil<sup>24</sup>. Upgrading the liquid products from biomass pyrolysis thus becomes necessary in solving this problem. A new method of upgrading bio-oil is proposed in our previous work<sup>25</sup>. The method is a process in which bio-oil is treated under pressure (2-6 MPa), temperature (280-380 °C) 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; hydrogen combines with oxygen to produce water. The catalysts were deactivated in the new bio-oil upgrading process because of carbon deposition on the surface of catalyst<sup>25</sup>. 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

**Dry mix method:** The water-gas shift catalyst (B206 low-temperature shift catalyst or B113 high-temperature shift catalyst, which was produced by Research Institute of Nanjing Chemical Industry Group) and hydrogenation catalyst (Pt/Al<sub>2</sub>O<sub>3</sub> or Ni-based catalyst) were crushed in 80-100 mesh and then mixed together according to a certain percentage.

**Impregnation method:** The water-gas shift catalyst (B206 low-temperature shift catalyst or B113 high-temperature shift catalyst, which was produced by Research Institute of Nanjing Chemical Industry Group) was crushed and sieved to a certain size, weighing a certain amount of shift catalyst and placing in a breaker. Nickel nitrate solution was dropped into the shift catalyst, stirring on a magnetic stirrer at the temperature of 40 °C for 12 h and then drying in the oven, finally, calcined at 500 °C for 5 h in the furnace.

**Experimental materials:** According to GC-MS analyzing, bio-oil is made up of more than 200 compounds. A number of researchers chosen a single-compound as bio-oil model to

examine the activity of catalyst. However, a single-comodel have different physical and chemical properties with bio-oil, which led to decrease the catalyst activity on the bio-oil upgrading. In present study, 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. The molecular formula of this model compound is similar with bio-oil. The composition of bio-oil model was given in Table-1.

Chemical name	Weight (g)	Chemical name	Weight (g)
Acid	80	Glycol	80
Propionaldehyde	80	Furfural	80
Acetone	80	Ethyl acetate	80
<i>m</i> -Cresol	80	Guaiacol	20
Ethanol	60	Water	340

**Experiment:** The tests of upgrading bio-oil model were carried out in the 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: 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. Second 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 lowered to room temperature.

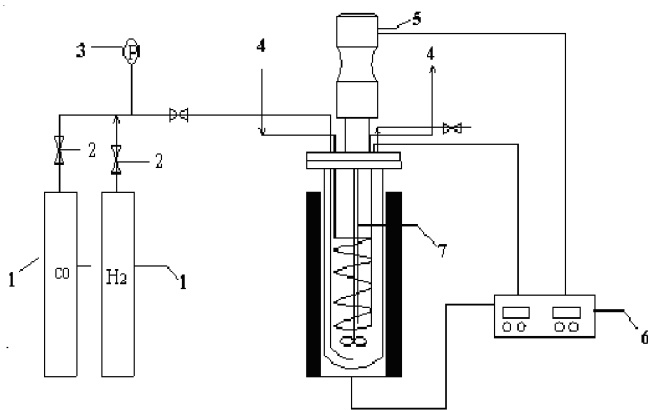


Fig. 1. Schematic diagram of experimental apparatus. 1. Cylinder; 2. Valve; 3. Gauge; 4. Condenser pipe; 5. Electric motor; 6. Control box; 7. Thermocouple

**Data analysis:** High quality bio-oil was the desirable product in upgrading bio-oil. The purpose of this work is to develop bi-functional catalyst and upgrade the bio-oil quality in an autoclave reactor under certain operation conditions. The equations used in this study can be shown as follows:

$$\text{Deoxygenation rate} = \frac{\text{Oxygen contents in bio-oil model} - \text{Oxygen content in the product}}{\text{Oxygen content in bio-oil model}}$$

$$\text{Dehydration rate} = \frac{\text{Water content in bio-oil model} - \text{Water content in the product}}{\text{Water content in bio-oil model}}$$

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

## RESULTS AND DISCUSSION

**Effect of different kinds of shift catalyst on deoxygenation rate and dehydration rate:** The test was carried out at pressure (6.0 Mpa), temperature (350 °C), speed (500 rpm),

reaction time (2 h),  $\frac{W_{\text{cat}}}{W_{\text{model of bio-oil}}} = \frac{1}{10}$ , solvent (tetralin, 50 mL) and model of bio-oil (50 mL). The results were shown in Fig. 2.

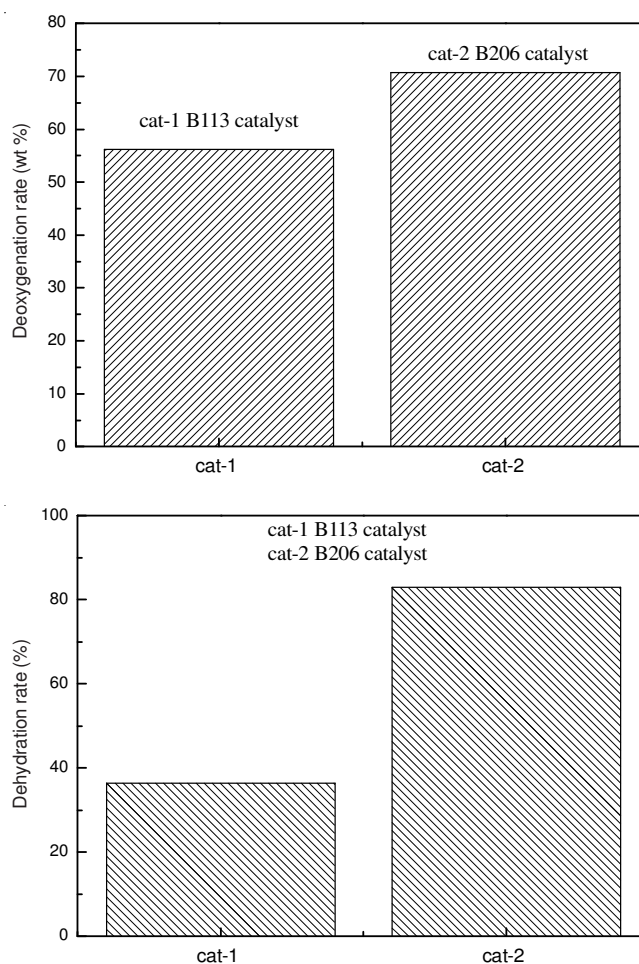


Fig. 2. Effect of different kinds of shift catalyst on deoxygenation rate and dehydration rate

As shown in Fig. 2, deoxygenation rate and dehydration rate of B206 low-temperature shift catalyst were significantly higher than that of B113 high-temperature shift catalyst. This may be due to B113 high-temperature shift catalyst showing good activity at 350-450 °C. In contrast, B206 low-temperature shift catalyst has a good catalytic performance at 250-300 °C. So B206 low-temperature shift catalyst was chosen as a shift component in the bi-functional catalyst.

**Effect of different kinds of hydrogenation catalyst on deoxygenation rate and dehydration rate:** The test was carried out at pressure (6.0 Mpa), temperature (350 °C), speed

(500 rpm), reaction time (2 h),  $\frac{W_{\text{cat}}}{W_{\text{model of bio-oil}}} = \frac{1}{10}$ , solvent (tetralin, 50 mL) and model of bio-oil (50 mL). The results were shown in Fig. 3.

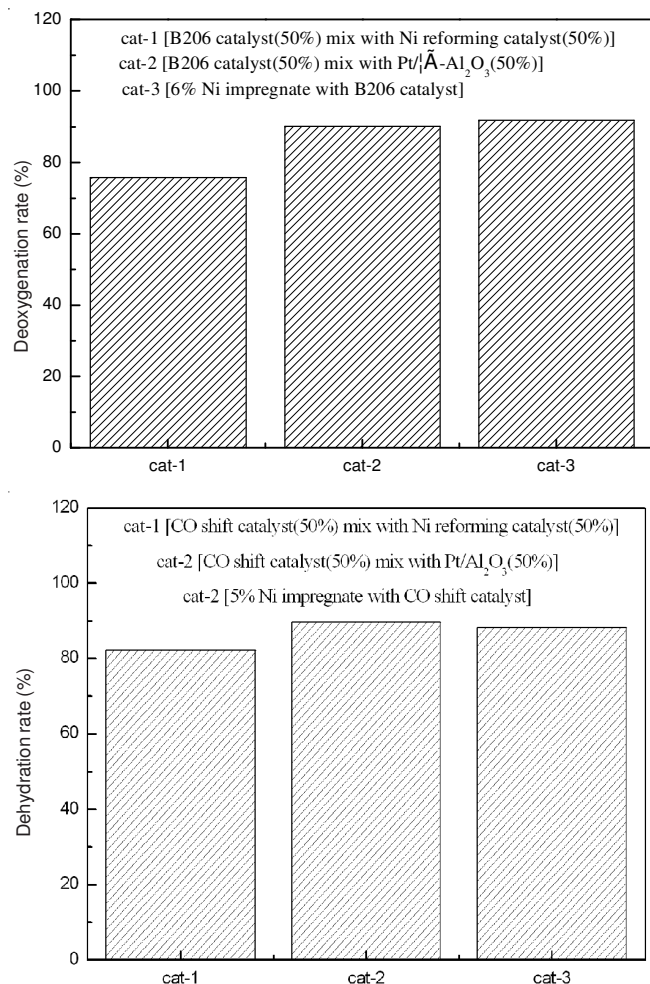


Fig. 3. Effect of different kinds of hydrogenation catalyst on deoxygenation rate and dehydration rate

As shown in Fig. 3, deoxygenation rate and dehydration rate of B206 catalyst (50 %) mixed with Ni reforming catalyst (50 %) were significantly lower than that of B113 catalyst mixed with Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 6 % Ni impregnated with B206 catalyst. The bi-functional catalyst, which was produced by impregnation method, showed the highest activity. This may be due to the active component contacting tightly in the process of impregnation. B113 catalyst mixed with Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> had a good activity, but Pt was expensive. So, the bi-functional catalyst (produced by impregnation method) was the optimum catalyst.

**Effect of different content of Ni on deoxygenation rate and dehydration rate:** In this part, the reaction was carried out at pressure (6.0 Mpa), temperature (350 °C), speed (500

rpm), reaction time (2 h),  $\frac{W_{\text{cat}}}{W_{\text{model of bio-oil}}} = \frac{1}{10}$ , solvent

(tetralin, 50 mL) and model of bio-oil (50 mL). The results were shown in Fig. 4.

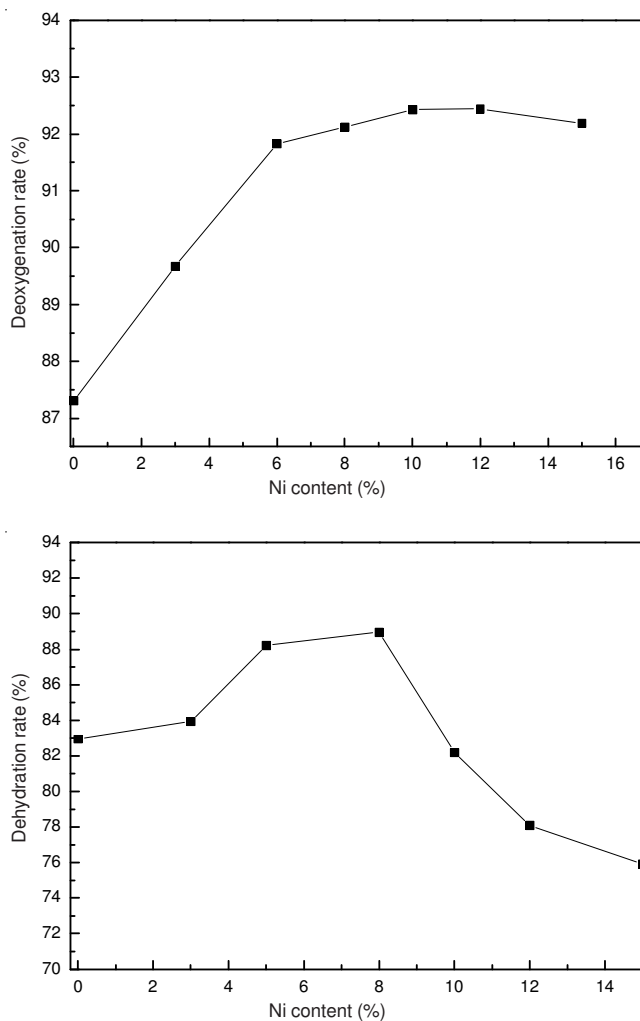


Fig. 4. Effect of different content of Ni on deoxygenation rate and dehydration rate

The results shown in Fig. 4 indicated deoxygenation rate and dehydration rate increased with the increase of Ni content in the bi-functional at first and then decreased when the content of Ni was more than 6 %. That is to say, deoxygenation rate and dehydration rate achieved a maximum. 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. The higher Ni content had a favour on hydrogenation reaction. On the contrary, with the Ni content in the bi-functional catalyst 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 bi-functional catalyst showed the highest activity for deoxygenation in the CO/H<sub>2</sub>O system, the deoxygenation rate was up to 92 % and the dehydration rate was 89 % after upgrading.

## 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. The bi-functional catalyst, which was produced by the mixed method, had a lower activity than that of catalyst produced by impregnation method. This may be due to the active component contacting tightly in the process of impregnation. 6 % Ni in the bi-functional catalyst showed the highest activity for deoxygenation in the CO/H<sub>2</sub>O system, the deoxygenation rate was up to 92 % and the dehydration rate was 89 % after upgrading.

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