Upgrading of fast pyrolysis liquid fuel from biomass over Ru/γ-Al2O3 catalyst

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ABSTRACT

Biomass is one of the important renewable energy. More attention has been paid on conversion of biomass and the upgrading of its products. In this paper, the bio-oil was prepared by pyrolysis of pine sawdust in fast pyrolysis installation. A series of ruthenium catalysts were prepared for the upgrading of bio-oil. The catalytic activity was evaluated by the reaction of the model compound (acetic acid) under 3 MPa hydrogen pressure. The effects of Ru-loading and second metal addition on the catalytic activity were investigated. The 0.5Ru/γ-Al2O3 catalyst with 0.5%Co addition exhibited the highest activity, giving the highest conversion of acetic acid (30.98%). After upgrading over this catalyst, the properties of the pyrolysis bio-oil were improved. The content of the esters increased by 2-fold in the upgraded oil than in the raw one. The GC–MS spectrometry analysis showed that not only the hydrogenation but also the esterification happened in the bio-oil over the CoRu/γ-Al2O3 catalyst. Results indicate that it is possible to improve the properties of bio-oil by hydrotreating and esterifying carboxyl groups.

The purpose of this paper was to investigate a new method for upgrading bio-oil, which needs mild conditions. Ru catalysts were prepared for the upgrading of fast pyrolysis bio-oil because it has better carbonyl hydrogenation activity and selectivity [18]. The effects of Ru loading and second metal addition on the catalytic activity of Ru/γ-Al2O3 catalysts were investigated. The bio-oil’s properties, element compositions and components were tested before and after upgrading process. The mechanism was also discussed.

1. Introduction

Biomass resources include wood wastes, agricultural crops and their waste byproducts, municipal solid waste, animal wastes, waste from food processing and aquatic plants and algae [1]. Being one of the important renewable energy, more attention has been paid on its conversion and the upgrading of its products [2–4]. Biomass, as a renewable material that has a negligible content of sulfur, nitrogen and ash, is supposed to be very clean. The fast pyrolysis of biomass has aroused great attention in recent years. However, bio-oil has disadvantages such as high viscosity, thermal instability, corrosiveness, and chemical complexity, which set up many obstacles before its full utilization [5,6]. The recent upgrading techniques include hydrodeoxygenation [7–11], catalytic cracking of pyrolysis vapors [11], emulsification [12,13], steam reforming [14,15], extracting chemicals from the bio-oils, esterification [16,17], etc.

Hydrotreatment of bio-oil over heterogeneous catalysts has been studied and it is shown that the caloric value and storage stability increased dramatically. The process conditions for hydro-treatment of bio-oil are rather severe (350–450°C, 5–15 MPa), leading to the formation of substantial amounts of gases and undesirable char. Thus there is a strong incentive to develop new catalysts and new ways to operate at lower temperature and hydrogen pressure for the upgrading of bio-oil.

The bio-oil was prepared by the fast pyrolysis of pine sawdust (40–60 mesh). The proximate and ultimate analysis of the pine sawdust is listed in Table 1. The liquid product obtained by fast pyrolysis pine sawdust was the upgraded feedstock.

2. Experimental section

2.1. Experiment material

The bio-oil was prepared by the fast pyrolysis of pine sawdust (40–60 mesh). The proximate and ultimate analysis of the pine sawdust is listed in Table 1. The liquid product obtained by fast pyrolysis pine sawdust was the upgraded feedstock.

2.2. Catalysts preparation

Ru/γ-Al2O3 catalysts were prepared by wet impregnating γ-Al2O3 with different RuCl3 6H2O aqueous solutions. The catalysts contained 0.2, 0.5, 0.7 and 1.0 wt.% Ru, separately. The solution was evaporated while the residue was dried at 120°C and then calcined in the air at 450°C.

The CeRu/γ-Al2O3 catalyst was prepared by wet impregnating γ-Al2O3 with the RuCl3 6H2O and Ce(NO3)3 6H2O mixed solution,
followed by drying and calcinating at 450°C. The catalyst contained 0.5 wt.% Ru and 0.5 wt.% Ce. In the same way, we got the catalysts of PtRu/γ-Al2O3, NiRu/γ-Al2O3, MoRu/γ-Al2O3, ZrRu/γ-Al2O3, LaRu/γ-Al2O3 and CoRu/γ-Al2O3.

2.3. Apparatus and method

The fast pyrolysis experimental apparatus is shown in Fig. 1. The experimental device mainly consists of a hopper, a screw feeder, an electric heater, a fluidized-bed reactor, one cyclone, two condensers, and an oil collector, as well as some thermocouples and pressure meters. The hopper is used to contain feedstock. The screw feeder is used to control the feeding rate. The fluidized-bed reactor has a height of 131 cm and a diameter of 12 cm, in which the biomass feedstock is rapidly heated for pyrolysis. The electric heater can pre-heat the nitrogen to the temperature of 300°C before entering into the fluidized-bed reactor. The cyclone is used to separate solid particles such as charcoal and ash from the hot gas. The condensers are equipped with cold water and a heat exchanger. The condensers can quickly cool the cleaned hot gas into a liquid. Thermocouples and pressure meters are used to monitor and control the pyrolysis system.

The fast pyrolysis was run at the optimum condition [19]. The characteristics of the fast pyrolysis bio-oil are shown in Table 2. All the upgrading experiments were carried out in a 250 ml autoclave with stirrer and water-cooling coil. The schematic diagram is shown in Fig. 2.

For each run, 0.50 g catalyst was loaded in the reactor per 10 ml acetic acid or bio-oil. After air being displaced, the cold H2 pressure was raised to 3 MPa. An automatic controller was used to control the temperature and revolution of the stirrer. The model reaction was carried out at 200°C. The upgrading of bio-oil was carried out at 100°C. The liquid products were sampled after 2 h and measured quantitatively by NaOH standard solution titration in model reaction.

2.4. Analysis

The conversion of acetic acid was measured quantitatively by NaOH standard solution titration. By the titration method, the acetic acid conversion was calculated by applying the equation: conversion = (1 – V/V0) × 100%, in which V and V0 are the volumes of standard NaOH solution consumed in neutralizing 0.5 mL solution sampled in the process and at the beginning of the reaction to change the phenolphthalein indicator pink, respectively. The products were measured by the internal standard method through GC2010 (Shimadzu, FID, N2 carrier gas, column: DB-1HT 30 m × 0.25 mm × 0.1 μm), with isoamyl acetate as the internal standard to discuss the mechanism reaction and calculate the content of the product in the model component.

For the bio-oil, the water content was determined by the Karl Fischer titration (ASTM D1744, GB11146-89), which was performed by using Metrohm 787 KF Titrino. The acidity was evaluated a PHC-3C precision pH-meter. The gas chromatography–mass spectrometry (Shimadzu GCMS-QP2010) was conducted to analyze the composition of bio-oil. The separation was realized on a column of DB-5 MS, 30 m × 0.25 mm × 0.1 μm, and the oven temperature program was 40°C (holding for 8 min) at 6°C/min to 280°C (holding for 30 min).

![Fig. 1. Fast pyrolysis experimental apparatus.](image_url)
3. Result and discussion

3.1. Catalytic activities

3.1.1. Effect of Ru content on catalytic activity

The effect of Ru content on the catalytic activity is listed in Table 3. It showed that acetic acid barely converted under 3 MPa hydrogenation and hydrogenolysis/hydrocracking of tetra-

### Table 3
Effect of Ru content on catalytic activity.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion of acetic acid (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2Ru/γ-Al2O3</td>
<td>11.95</td>
</tr>
<tr>
<td>0.5Ru/γ-Al2O3</td>
<td>16.77</td>
</tr>
<tr>
<td>0.7Ru/γ-Al2O3</td>
<td>16.79</td>
</tr>
<tr>
<td>1.0Ru/γ-Al2O3</td>
<td>16.66</td>
</tr>
</tbody>
</table>

3.1.2. Catalytic activity of modified Ru/γ-Al2O3 catalyst

The activities of modified catalysts of Ru/γ-Al2O3 are listed in Table 4. With the addition of Ce, Pt, Ni, Mo, Zr, La and Co, the activity of catalysts was promoted correspondingly. The conversions of acetic acid increased when the catalyst was present. With the increase of Ru content, the conversion of acetic acid ascended. It increased slowly with Ru content was over 0.5 wt.%.

### Table 4
Effect of adding promoters on catalytic activity.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion of acetic acid (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2Ru/γ-Al2O3</td>
<td>16.77</td>
</tr>
<tr>
<td>CeRu/γ-Al2O3</td>
<td>16.87</td>
</tr>
<tr>
<td>PtRu/γ-Al2O3</td>
<td>17.46</td>
</tr>
<tr>
<td>NiRu/γ-Al2O3</td>
<td>18.68</td>
</tr>
<tr>
<td>MoRu/γ-Al2O3</td>
<td>18.19</td>
</tr>
<tr>
<td>ZrRu/γ-Al2O3</td>
<td>18.64</td>
</tr>
<tr>
<td>LaRu/γ-Al2O3</td>
<td>24.06</td>
</tr>
<tr>
<td>CoRu/γ-Al2O3</td>
<td>30.98</td>
</tr>
</tbody>
</table>

T = 200 °C, P = 3 MPa, t = 2 h.

3.1.3. Mechanism of the hydrotreating reaction of acetic acid

Fig. 3 shows the change of acetic acid before and after upgrading reaction. The first peak (Rt = 5.49 min) in Fig. 3a is the characteristic peak of acetic acid. The second one (Rt = 10.27 min) is the inner-labeled compound isoamyl acetate characteristic peak. In the Fig. 3b, before the peak of acetic acid, there appeared a pinnacle (Rt = 5.02), which was identified the characteristic peak of ethyl acetate. Ethyl acetate should come from acetic acid and alcohol. As there was no alcohol in reactants, the alcohol should come from acetic acid reduction.

It is reported that Ru catalyst can be found wide applications in hydrogenation, hydrodechlorination [22], hydodesulfurization [23], etc. For the affinity behavior on heteroatom of Ru, the catalysts are used in the hydrogenation of α,β-unsaturated aldehydes [24], carboxylic component, esters [25], single or multiple C–N bonds [26], etc. Li [27] used Ru-Pd/γ-Al2O3 catalyst for the hydrogenation and methyl esterification of α-furfurancarboxylic acid. In this experiment, the hydrogenation and esterification were carried out over the CoRu/γ-Al2O3 catalyst.

In this upgrading reaction, the hydrogen pressure was relative low. The acetic acid was activated and deoxidized, generating water and acetaldehyde, which was hydrogenated farther to attain alcohol. Esterification did occur in the reactor for the existence of ethyl acetate. There was no signal of alcohol in the system after the reaction. That might because there was excessive acetic acid existent in the reactor. The conversion of alcohol could reach 100%. The reactions might happen as the Eq. (1)–(3) in process of upgrading.

\[
\text{CH}_3\text{COOH} + \text{H}_2 \rightarrow \text{CH}_3\text{CHO} + \text{H}_2\text{O} \tag{1}
\]

\[
\text{CH}_3\text{CHO} + \text{H}_2 \rightarrow \text{CH}_3\text{CH}_2\text{OH} \tag{2}
\]

\[
\text{CH}_3\text{COOH} + \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{COOCH}_2\text{CH}_3 + \text{H}_2\text{O} \tag{3}
\]

3.2. Upgrading of fast pyrolysis bio-oil

3.2.1. Properties of bio-oil

The properties of bio-oils are listed in Table 5. If there were no changes. But according to Table 5, the properties should have no changes. The reactions might happen as the Eq. (1)–(3) in process of upgrading.

\[
\text{CH}_3\text{COOH} + \text{H}_2 \rightarrow \text{CH}_3\text{CHO} + \text{H}_2\text{O} \tag{1}
\]

\[
\text{CH}_3\text{CHO} + \text{H}_2 \rightarrow \text{CH}_3\text{CH}_2\text{OH} \tag{2}
\]

\[
\text{CH}_3\text{COOH} + \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{COOCH}_2\text{CH}_3 + \text{H}_2\text{O} \tag{3}
\]
The contents of C and H increased from 53.61% and 6.25% to 53.76% and 6.56%, separately.

### 3.2.2. Composition of bio-oil

Bio-oil is a complex mixture highly oxygenated with a great amount of large-size molecules, which nearly involve all species of oxygenated organics, such as esters, ethers, aldehydes, ketones, phenols, organic acids and alcohols. The GC–MS spectrums of the raw bio-oil and upgraded one are illustrated in Fig. 4.

From Fig. 4, we could find out that there was much difference between the raw oil and the upgraded one. For example, the obvious peaks at time = 41.70 and 42.25 min in Fig. 4b did not appear in Fig. 4a.

<table>
<thead>
<tr>
<th>Properties of raw bio-oil and upgraded one.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>pH</td>
</tr>
<tr>
<td>Water content (%)</td>
</tr>
<tr>
<td>Calorific value (MJ/kg)</td>
</tr>
<tr>
<td>Element compositions</td>
</tr>
<tr>
<td>C</td>
</tr>
<tr>
<td>H</td>
</tr>
<tr>
<td>O</td>
</tr>
<tr>
<td>N</td>
</tr>
</tbody>
</table>

\(T = 100 \, ^\circ \text{C}, P = 3 \, \text{MPa}, t = 2 \, \text{h.}\)

Fig. 3. (a) GC spectrum of acetic acid before hydrotreating. (b) GC spectrum of acetic acid after hydrotreating.

Fig. 4. (a) GC–MS spectrum of raw fast prolysis bio-oil. (b) GC–MS spectrum of upgraded fast prolysis bio-oil.
Increased from 9.09% to 17.56% over CoRu/\(\gamma\)-Al\(_2\)O\(_3\) catalyst, both hydrotreatment and esterification happened during the upgrading of bio-oil. The content of esters increased by 2-fold. Results indicate that it is possible to improve the properties of bio-oil by hydrotreating and esterifying carboxyl group.

### Acknowledgments

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### References


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**Table 6** Percent area of acids and esters of raw bio-oil and upgraded one.

<table>
<thead>
<tr>
<th>Component</th>
<th>Raw bio-oil</th>
<th>Upgraded bio-oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic acids (%)</td>
<td>10.44</td>
<td>9.09</td>
</tr>
<tr>
<td>Esters (%)</td>
<td>8.62</td>
<td>17.56</td>
</tr>
</tbody>
</table>

T = 100 °C, P = 3 MPa, t = 2 h.

**Table 7** Corresponding components in raw bio-oil and upgraded one.

<table>
<thead>
<tr>
<th>Component</th>
<th>Raw bio-oil</th>
<th>Upgraded bio-oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid</td>
<td>Ethyl acetate</td>
<td></td>
</tr>
<tr>
<td>Formaldehyde/formic acid</td>
<td>Methyl alcohol</td>
<td></td>
</tr>
<tr>
<td>Propanoic acid</td>
<td>Propanoic acid, propyl ester</td>
<td></td>
</tr>
<tr>
<td>Acetic acid + formaldehyde/formic acid</td>
<td>Acetic acid, methyl ester</td>
<td></td>
</tr>
<tr>
<td>Butanal + acetic acid</td>
<td>Acetic acid, butyl ester</td>
<td></td>
</tr>
<tr>
<td>2,3-Butanediol</td>
<td>3-Hydroxy-2-butanone</td>
<td></td>
</tr>
</tbody>
</table>

T = 100 °C, P = 3 MPa, t = 2 h.

**Fig. 4a.** According to analysis results, they were the signals of octanoic acid, 2-octyl ester and butanediolic acid, methyl-, bis(1-methylpropyl) ester. They did not exist in the raw oil. The peak at time = 1.86 min became lower and narrow in Fig. 4b than in Fig. 4a, and it was the signal of formic acid, whose content decreased after upgrading.

The comparison on the spectroscopy is shown in Table 6 and validated the remarkable variation on the composition of bio-oil considering the source material [16]. In this fast pyrolysis bio-oil, the percent area of acids reached to 10.44% in the GC–MS area. But after upgrading, it decreased to 8.62%. The area of esters was increased from 9.09% to 17.56% over CoRu/\(\gamma\)-Al\(_2\)O\(_3\) catalyst, including esters based on volatile acids, such as formate, acetate and propanoic acid. The acids content decreased, meanwhile the ester content increased by nearly 2-fold. Esters, being one of good fuel, are also a high grade valuable chemical. Over the catalyst, if the organic acids could convert to esters during the upgrading process, it could be a good way to produce esters, reduce the acid of bio-oil and expand the utilization of bio-oil. Results indicate that it is possible to improve the properties of bio-oil by hydrotreating and esterifying carboxyl groups.

The reaction which might happen in the bio-oil was illustrated in Table 7. From Table 7, we can find out that the model reaction did happen during the upgrading progress. And the model reactions did not limited to acetic acid, but applied to other kinds of acids. Ethyl acetate, propanoic acid, propyl ester, acetic acid methyl ester, etc. could be found in the upgraded bio-oil. The organic acids, aldehydes and ketones might convert to alcohols over the catalyst under the atmosphere of hydrogen over CoRu/\(\gamma\)-Al\(_2\)O\(_3\) catalyst. Methyl alcohol, 3-hydroxy-2-butanone, etc. could be found in the upgraded bio-oil. After the acids being deoxidized and hydrogenated to alcohols, it could also react with other acids to yield esters. Acetic acid methyl ester might form in this way.

**4. Conclusion**

Acetic acid can be hydrodeoxygenated and esterified over Ru/\(\gamma\)-Al\(_2\)O\(_3\) catalysts under mild condition. Adding second metal can promote the activity of the catalysts. Co as a good addition could promote the activity of Ru/\(\gamma\)-Al\(_2\)O\(_3\) catalyst obviously. The conversion of acetic acid can reach 30.98%.

After upgrading, the pH value of the bio-oil increased from 2.33 to 2.47. The water content increased from 35.52% to 38.55%. The calorific value increased from 13.96 MJ/kg to 14.09 MJ/kg. The C and H contents increased from 53.61% and 6.25% to 53.76% and 6.56%, separately. Over the CoRu/\(\gamma\)-Al\(_2\)O\(_3\) catalyst, both hydrotreatment and esterification happened during the upgrading of bio-oil. The content of esters increased by 2-fold. Results indicate that it is possible to improve the properties of bio-oil by hydrotreating and esterifying carboxyl group.

