Comparative Study on Microwave Co-pyrolysis Products of Low-Rank Coal under H₂ and N₂ Atmosphere

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Abstract—The microwave pyrolysis of the low-rank coal is a new technology, which solves the utilization problems of coal cleaning conversion. On basis of experiments, this paper conducted comparative study on microwave co-pyrolysis products of low-rank coal under H₂ and N₂ atmosphere, respectively. The composition and content of tar and bluecoke were analyzed by gas chromatography-mass spectrometry and fourier transform infrared spectrometer. The results indicated that compared with N₂ atmosphere, the yield of liquid products (tar and pyrolysis water) obtained under H₂ atmosphere was higher than 7.8 wt.%, the bluecoke yield was lower than 4.2 wt.%; The content of S element in the bluecoke obtained under H₂ atmosphere was 0.24 wt.% to meet Bluecoke Standard S-1 Grade, and the N element content was just 0.48 wt.%. Furthermore, the content of –OH, C=C and –C=O functional groups in the bluecoke were higher; The alkanes compound content in tar obtained under H₂ atmosphere was 13.0 wt.% higher than that under N₂ atmosphere, meanwhile, the aromatic hydrocarbons compound content was 34.5 wt.% lower than that under N₂ atmosphere.

Keywords—Low-rank coal; Microwave co-pyrolysis; Products; Hydrogen; Nitrogen.

I. INTRODUCTION

Coal is still a major energy source for China in the foreseeable future. Pyrolysis, an intermediate stage in various conversion processes such as liquefaction, gasification and combustion, is an important method of clean utilization of coal. China is rich in low-rank coal resources, accounting for more than 45% of the total proven reserves of coal resources [1]. The medium-low temperature pyrolysis of low-rank coal to realize separation and transformation of its gas, liquid and solid components, thus making for further upgrading utilization of three-phase products, is considered to be the best way to increase the value-added of its products. However, the current mainstream pyrolysis production technology generally has a certain particle size requirements for raw coal, lower yield and poorer quality of coal tar, and low-value coal-gas content (e.g., H₂, CH₄, and CO) [2]. Therefore, how to make full use of low-rank coal is still a hot topic at present on the development of coal chemical industry. Numerous scholars through lots of experimental studies have found that pyrolysis conditions of coal, such as pyrolysis terminal temperature, heating rate, pressure, atmosphere, particle size, catalyst, coal and reactor types had strongly influence on the yield and composition of pyrolysis products. Especially, reaction atmosphere had much significantly influence on the composition and distribution of pyrolysis products.
Researchers [3-5] have found that: coal pyrolysis under hydrogen-rich atmosphere could produce high heat-value gas, high yield and quality tar, clean semi-coke and better chemical desulfurization effect. Hydropyrolysis (HyPy) is a pyrolysis process under hydrogen. Compared with pyrolysis under inert gas, the quantity and quality of tar are improved, and low sulfur char is produced in HyPy due to that the thermally released free radicals can be stabilized by capturing hydrogen to produce tar with low molecular weight compounds and that most sulfur in coal can be removed as gaseous H₂S[6-8]. Thus, HyPy provides a route for the production of liquid from coals and extensive studies on HyPy have been reported.

II. EXPERIMENTAL

A. Coal samples

Low-rank coal was used for the experimental material, it was cruched and sized to a range from 5 to 10 mm, followed by dewatering at 100 °C for 12h in a vacuum oven before being used for pyrolysis experiments. The proximate and ultimate analyses of coal samples are showed in TABLE 1.

<table>
<thead>
<tr>
<th>Proximate analysis</th>
<th>Ultimate analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>A</td>
</tr>
<tr>
<td>3.41</td>
<td>2.64</td>
</tr>
</tbody>
</table>

B. Experimental apparatus and methods

Experimental apparatus of low-rank coal microwave co-pyrolysis under H₂ and N₂ atmosphere are shown in Fig. 1. It was mainly made up of the carrier gas system, microwave equipment, product cooling system, gas collecting system and temperature recording system. A certain amount of coal samples were fed into a custom-designed quartz tube reactor with the size of 55mm in diameter and 600mm in length. H₂ and N₂ were provided by gas cylinder, the pressure reduction valve and rotor flow meter could provide a relatively stable pressure environment. Weight difference method was adopted to calculate the solid and liquid products (tar and pyrolysis water) yield and weight loss rate of coal samples after the end of pyrolysis reaction. Related formulas were defined as Formula (1–3).

\[
Y_{\text{char}} = \frac{W_{\text{char}}}{W_0} \times 100\% 
\]

\[
Y_{L} = \frac{W_L}{W_0} \times 100\% 
\]

\[
\text{WLR} = \frac{(W_0 - W_{\text{char}})}{W_0} \times 100\% 
\]

\[
Y_{\text{char}}—\text{Yield of the bluecoke (wt.%)}; Y_{L}—\text{Yield of the liquid products (wt.%)}; \text{WLR}—\text{Weight loss rate of coal samples (wt.%)}; W_{\text{char}}—\text{Mass of the bluecoke (g)}; W_{0}—\text{Mass of the liquid products (g)}. 
\]

III. RESULTS AND DISCUSSION

A. Yield of pyrolysis products

The yield of pyrolysis products and weight loss rate of coal samples obtained under H₂ and N₂ atmosphere are showed in TABLE 2. It could be easily found that the yield of liquid products and bluecoke obtained under H₂ atmosphere were up to 25.8 wt.% and 61.6 wt.%, respectively. Compared with N₂ atmosphere, the liquid products yield increased by 7.8 wt.%, whereas the bluecoke yield decreased by 4.2 wt.%. It suggests that H₂ could contribute to the formation of liquid products during the coal pyrolysis.

<table>
<thead>
<tr>
<th>Item</th>
<th>H₂</th>
<th>N₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y_{\text{char}}</td>
<td>61.6</td>
<td>65.8</td>
</tr>
<tr>
<td>Y_{L}</td>
<td>25.8</td>
<td>18.0</td>
</tr>
<tr>
<td>WLR</td>
<td>38.4</td>
<td>34.2</td>
</tr>
</tbody>
</table>

B. Analysis of the bluecoke

The proximate and ultimate analyses of the bluecoke obtained under H₂ and N₂ atmosphere are showed in TABLE 3. According to the analyses of raw coal quality (TABLE 1), TABLE 3 shows that the volatile and H element content in the bluecoke obtained under H₂ and N₂ atmosphere decreased obviously, while the ash, fixed carbon and C element content increased significantly. Moisture evaporated rapidly, organic matter decomposed gradually, and minerals were enriched effectively during coal pyrolysis. According to China Bluecoke Standard Classification and quality grading for bluecoke[10], compared with N₂ atmosphere, the content of S element in the bluecoke obtained under H₂ atmosphere was 0.24 wt.% to meet Bluecoke Standard S-1 Grade, and the N element content was just 0.48 wt.%. It suggests that H₂ promoted desulfurization and denitrification during the coal pyrolysis. Fig. 2 shows FTIR spectra of the bluecoke obtained under H₂ and N₂ atmosphere. It can be seen that peak position of the bluecoke in FTIR spectra are basically the same, but larger differences exists in distinctive peak area. It indicates that pyrolysis atmosphere had stronger influence on the content of
distinctive functional groups in bluecoke. Compared to the standard FTIR spectra library, the peak at 3450 cm\(^{-1}\) was ascribed to the stretching vibration of –OH or –NH functional groups associated by hydrogen bond, –NH functional groups had little influence due to lower content of N element in low-rank coal, so –OH functional groups content may be higher due to more strongly peak position transformation. The peaks at 1600 cm\(^{-1}\) was attributed to the stretching vibration of aromatic ring C=C double bond and –C=O associated by hydrogen bond. It can be easily found that the content of –OH, C=C and –C=O functional groups in the bluecoke obtained under H\(_2\) atmosphere were higher than that under N\(_2\) atmosphere.

TABLE 3. Proximate and ultimate analyses of the bluecoke obtained under H\(_2\) and N\(_2\) atmosphere (wt.%, ad)

<table>
<thead>
<tr>
<th>Atmosphere</th>
<th>Proximate analysis</th>
<th>Ultimate analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(M)</td>
<td>(A)</td>
</tr>
<tr>
<td>H(_2)</td>
<td>2.84</td>
<td>8.12</td>
</tr>
<tr>
<td>N(_2)</td>
<td>1.10</td>
<td>7.28</td>
</tr>
</tbody>
</table>

Figure 2. FTIR spectra of the bluecoke obtained under H\(_2\) and N\(_2\) atmosphere

**C. Analysis of the tar**

Gas chromatography-mass spectrometry (GC-MS) data of tar obtained under H\(_2\) and N\(_2\) atmosphere are shown in Fig. 3. Coal tar is complex mixture composed of a variety of organic compounds, and GC-MS chromatograms show many chromatographic peaks without a single component of individual chromatographic peak. The tar was analyzed after separating water from liquid products. Main components content of the tar obtained under H\(_2\) and N\(_2\) atmosphere are given in TABLE 4. It can be seen in TABLE 4 that the alkanes compound content in tar obtained under H\(_2\) atmosphere was up to 45.2 wt.%. Whereas the aromatic hydrocarbons compound content was just 9.70 wt.%. The alkanes content in tar obtained under H\(_2\) atmosphere was 13.0 wt.% higher than that under N\(_2\) atmosphere, meanwhile, the aromatic hydrocarbons compound content was 34.5 wt.% lower than that under N\(_2\) atmosphere. It suggests that H\(_2\) is more conducive to the formation of light component in coal tar during the coal pyrolysis.

![Figure 3. GC-MS chromatograms of the tar obtained under H\(_2\) and N\(_2\) atmosphere](image)

TABLE 4. MAIN COMPONENTS CONTENT OF THE TAR OBTAINED UNDER H\(_2\) AND N\(_2\) ATMOSPHERE (WT.%)

<table>
<thead>
<tr>
<th>Atmosphere</th>
<th>Alkanes</th>
<th>Olefins</th>
<th>Aromatic hydrocarbons</th>
<th>Oxygen-containing functional groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)</td>
<td>45.2</td>
<td>3.40</td>
<td>9.70</td>
<td>17.9</td>
</tr>
<tr>
<td>N(_2)</td>
<td>32.2</td>
<td>7.50</td>
<td>44.2</td>
<td>8.90</td>
</tr>
</tbody>
</table>

IV. CONCLUSIONS

1) Compared with N\(_2\) atmosphere, the yield of liquid products (tar and pyrolysis water) obtained under H\(_2\) atmosphere increased by 7.8 wt.%, whereas the bluecoke yield decreased by 4.2 wt.%.

2) Compared with N\(_2\) atmosphere, the content of S element in the bluecoke obtained under H\(_2\) atmosphere was 0.24 wt.% to meet Bluecoke Standard S-1 Grade, and the N element content was just 0.48 wt.%. Furthermore, the content of –OH, C=C and –C=O functional groups in the bluecoke were higher.

3) The alkanes compound content in tar obtained under H\(_2\) atmosphere was 13.0 wt.% higher than that under N\(_2\) atmosphere, meanwhile, the aromatic hydrocarbons compounds content was 34.5 wt.% lower than that under N\(_2\) atmosphere.
ACKNOWLEDGMENT

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