Comparative Study on Microwave Co-pyrolysis Products of Low-Rank Coal under H_2 and N_2 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 H_2 and N_2 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 N_2 atmosphere, the yield of liquid products (tar and pyrolysis water) obtained under H_2 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 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; 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 compound content was 34.5 wt.% lower than that under N_2 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., H_2, CH_4, 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 H_2S[6-8]. Thus, HyPy provides a route for the production of 1iquid 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℃ 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 1 Proximate and ultimate analyses of coal samples (wt.%, ad)

Proximate analysis				**Ultimate analysis**				
M	***A***	***FC***	***V***	***C***	***H***	***N***	S_t	***O***
3.41	2.64	56.16	37.79	76.38	4.71	0.99	0.26	11.61

B. *Experimental apparatus and methods*

Experimental apparatus of low-rank coal microwave co-pyrolysis under H_2 and N_2 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. H_2 and N_2 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).

$$Y_{char}=W_{char}/W_0\times100\% \quad (1)$$

$$Y_L=W_L/W_0\times100\% \quad (2)$$

$$WLR=(W_0-W_{char})/W_0\times100\% \quad (3)$$

Y_{char}—Yield of the bluecoke (wt.%);Y_L—Yield of the liquid products (wt.%);WLR—Weight loss rate of coal samples (wt.%);W_0—Mass of coal samples before experiment (g);W_{char}—Mass of the bluecoke (g);W_L—Mass of the liquid products (g).

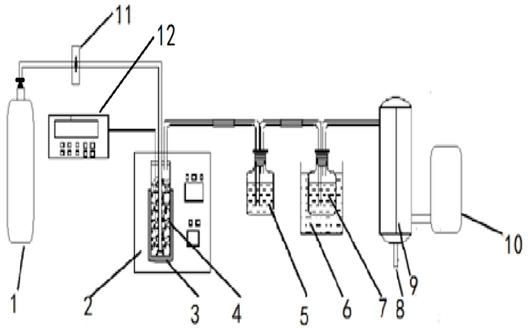


Figure 1. Experimental apparatus of low-rank coal microwave co-pyrolysis under H_2 and N_2 atmosphere[9]

1—Gas cylinder; 2—Microwave device; 3—Asbestos cover; 4—Quartz reactor; 5—Water bottle; 6—Ice bath; 7—Water bottle; 8—Tar collecting; 9—Tar trap; 10—Gas pocket; 11—Rotameter; 12—Temperature display.

III. RESULTS AND DISCUSSION

A. *Yield of pyrolysis products*

The yield of pyrolysis products and weight loss rate of coal samples obtained under H_2 and N_2 atmosphere are showed in TABLE 2. It could be easily found that the yield of liquid products and bluecoke obtained under H_2 atmosphere were up to 25.8 wt.% and 61.6 wt.%, respectively. Compared with N_2 atmosphere, the liquid products yield increased by 7.8 wt.%, whereas the bluecoke yield decreased by 4.2 wt.%. It suggests that H_2 could contribute to the formation of liquid products during the coal pyrolysis.

TABLE 2. Yield of pyrolysis products and WLR of coal samples under CG and N_2 atmosphere(wt.%)

Item	H_2	N_2
Y_{char}	61.6	65.8
Y_L	25.8	18.0
WLR	38.4	34.2

B. *Analysis of the bluecoke*

The proximate and ultimate analyses of the bluecoke obtained under H_2 and N_2 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 H_2 and N_2 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 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.%. It suggests that H_2 promoted desulfurization and denitrification during the coal pyrolysis. Fig. 2 shows FTIR spectra of the bluecoke obtained under H_2 and N_2 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 3450cm^{-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)

Atmosphere	**Proximate analysis**				**Ultimate analysis**			
	M	***A***	***FC***	***V***	***C***	***H***	***N***	S_t
H_2	2.84	8.12	84.9	4.10	86.0	0.47	0.48	0.24
N_2	1.10	7.28	86.9	4.71	86.4	1.16	1.02	0.32

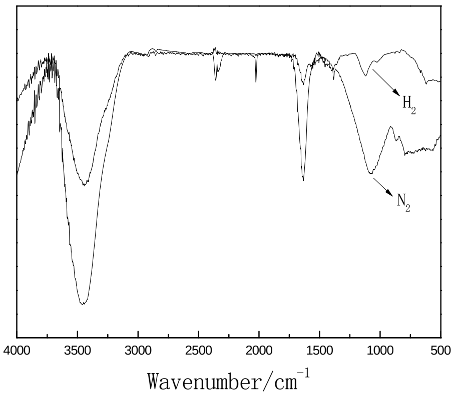
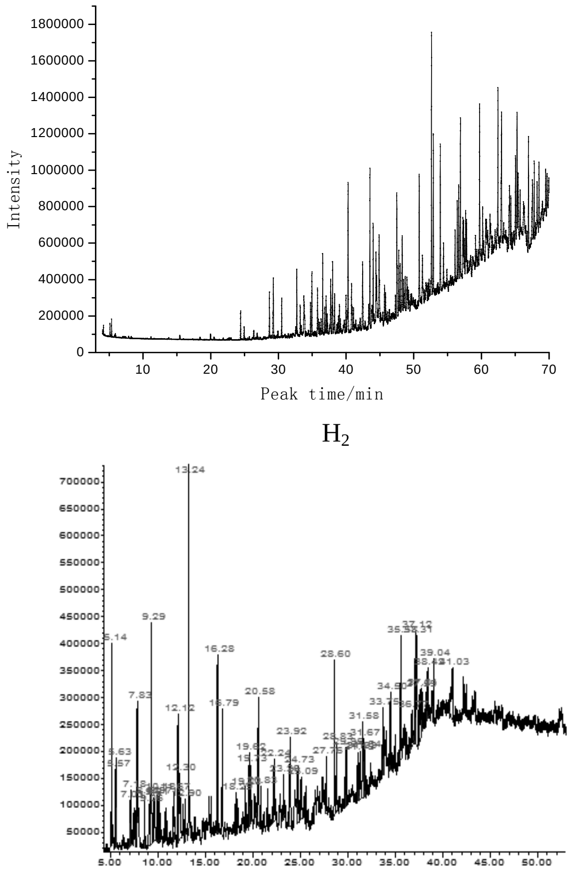


Figure 2. FTIR spectra of the bluecoke obtained under H_2 and N_2 atmosphere

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.



H_2

N_2

Figure 3. GC-MS chromatograms of the tar obtained under H_2 and N_2 atmosphere

TABLE 4. MAIN COMPONENTS CONTENT OF THE TAR OBTAINED UNDER H2 AND N2 ATMOSPHERE (WT.%)

Atmosphere	**Alkanes**	**Olefins**	**Aromatic hydrocarbons**	**Oxygen-containing functional groups**
H_2	45.2	3.40	9.70	17.9
N_2	32.2	7.50	44.2	8.90

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.

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