Comparative Study on Microwave Co-pyrolysis Products of Low-Rank Coal under Circulating Gas and N_2 Atmosphere

J.ZHOU[1] ,L.WU[2] ,Z. YANG [3] ,X.F. LIU [4] ,Y.H. SONG[5] & X.C. ZHAO[5]

[1]School of Metallurgical Engineering, Xi' an University of Architecture and Technology, Shaanxi Province Metallurgical Engineering and Technology Research Centre, Xi'an, Shaanxi, P.R. China

[2]Xinjiang Chemical Engineering Design & Research Institute Co., Ltd., Urumqi, Xinjiang, P.R. China

[3]School of Metallurgical Engineering, Xi' an University of Architecture and Technology, Xi'an, Shaanxi, P.R. China

[4]Yulin Science &Technology Information Research Institute, Yulin, Shaanxi, P.R. China

[5]School of Metallurgical Engineering, Xi' an University of Architecture and Technology, Shaanxi Province Metallurgical Engineering and Technology Research Centre, Xi'an, Shaanxi, P.R. China

KEYWORDS: Low-rank coal; Microwave co-pyrolysis; Products; Circulating gas; Nitrogen.

ABSTRACT: Microwave pyrolysis is a new research method for deeply processing of low-rank coal. On basis of experiments, this paper conducted comparative study on microwave co-pyrolysis products of low-rank coal under circulating gas (CG) 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 CG atmosphere was higher than 8.0 wt.%, whereas the bluecoke yield was lower than 4.4 wt.%; The content of S element in the bluecoke obtained under CG atmosphere was 0.16 wt.% to meet Bluecoke Standard S-1 Grade, and the N element content was just 0.67 wt.%. Furthermore, the content of –OH、C=C and –C＝O functional groups in the bluecoke were higher; The alkanes compounds content in tar obtained under CG atmosphere was 8.10 wt.% higher than that under N_2 atmosphere, meanwhile, the aromatic hydrocarbons compounds content was 37.4 wt.% lower than that under N_2 atmosphere.

Introduction

With the development of economy, the shortage of energy resources is increasingly aggravating, the economic value of low-rank coal and its upgrading technology have received more and more attentions. Pyrolysis at medium-low temperature has been considered as one of the effective methods to upgrading of low-rank coal, which can produce gas (coal gas), liquid (tar) and solid phases (semi-coke or coke) or other valuable chemicals to increase the value-added of its products. Development of coal-to-liquids is an important approach to resolve the shortage of petroleum resources in China. Coal pyrolysis at lower temperature is the most economic energy conversion efficiency for making liquid fuels from coal. Coal hydropyrolysis can effectively improve yield of tar during coal pyrolysis. Hence, the foundation and applied research of coal hydropyrolysis has been gived extensive attention. Researchers [1,2] have found that: coal pyrolysis under hydrogen-rich atmosphere could produce high heat-value gas, high yield and quality tar, clean semi-coke and good chemical desulfurization effect. However, hydropyrolysis is not a feasible process due to the high-cost and narrow source of pure hydrogen. Therefore, much cheaper and accessible coke-oven gas (COG) and syngas (SG) as pyrolysis atmosphere in stead of pure hydrogen have been proposed [3]. Braekman-Dalllleux et al. [4,5] investigated the effect of temperature and coke-oven gas composition on product yield of coal hydropyrolysis and semi-coke characteristics, and confirmed the feasibility of the coke-oven gas in stead of pure hydrogen. In recent years, microwave pyrolysis technology of coal gradually developed as a new type of clean coal carbonization technology [6]. Therefore, working on the coal and circulating gas (CG) microwave co-pyrolysis [7] experimental research is a beneficial attempt to realize upgrading of low-rank coal effectively, which has important practical significance. This paper conducted comparative study on microwave co-pyrolysis products of low-rank coal under CG and N_2 atmosphere in the optimal pyrolysis process conditions.

EXPERIMENTAL

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	56.2	37.8	76.4	4.71	0.99	0.26	11.6

Experimental apparatus and methods

Experimental apparatus of low-rank coal microwave co-pyrolysis under circulating gas (CG) and N_2 atmosphere are shown in Figs.1 and 2, respectively. 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. 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.

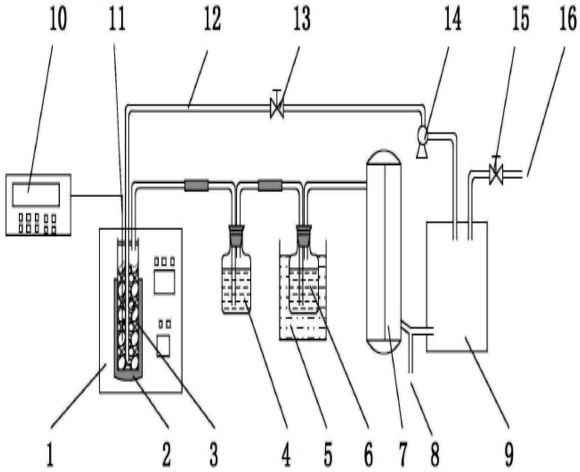


Figure 1. Experimental apparatus of low-rank coal microwave co-pyrolysis under CG atmosphere

1—Microwave device;2—Ceramic insulation sleeve;3—Quartz reactor;4—First-order absorption cooler;5—Circulating cooling pump;6—second-stage absorption cooler;7—Electrical tar precipitator;8—T-branch pipe;9—Gas collecting cabinet;10—Intelligent temperature controller;11—Thermocouple;12—Intake-tube;13—Loop valve;14—Explosion proof air pump;15—Outlet valve;16—Outlet pipe

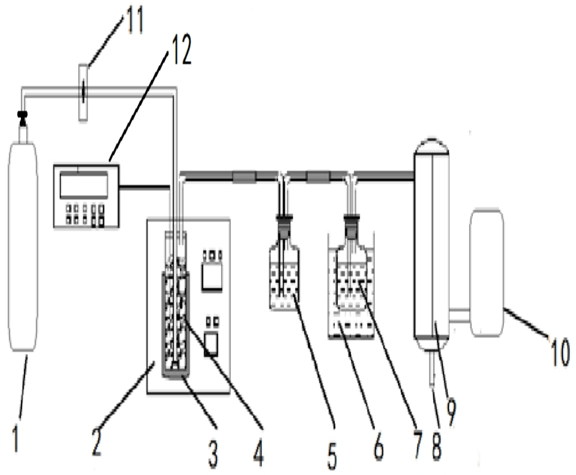


Figure 2. Experimental apparatus of low-rank coal microwave co-pyrolysis under N_2 atmosphere

1—N_2 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

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).

RESULTS AND DISCUSSION

Yield of pyrolysis products

The yield of pyrolysis products and weight loss rate of coal samples obtained under CG and N_2 atmosphere are showed in Table 2. It could be easily found that the yield of liquid products and bluecoke obtained under CG atmosphere were up to 26.0 wt.% and 61.4 wt.%, respectively. Compared with N_2 atmosphere, the liquid products yield increased by 8.0 wt.%, whereas the bluecoke yield decreased by 4.4 wt.%. It suggests that CG 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	CG	N_2
Y_{char}	61.4	65.8
Y_L	26.0	18.0
WLR	38.6	34.2

Analysis of the bluecoke

The proximate and ultimate analyses of the bluecoke obtained under CG 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 CG 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[8], compared with N_2 atmosphere, the content of S element in the bluecoke obtained under CG atmosphere was 0.16 wt.% to meet Bluecoke Standard S-1 Grade, and the N element content was just 0.67 wt.%. Fig.3. shows FTIR spectra of the bluecoke obtained under CG and N_2 atmosphere. 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 CG atmosphere were higher than that under N_2 atmosphere.

Table 3. Proximate and ultimate analyses of the bluecoke obtained under CG and N_2 atmosphere (wt.%, ad)

Atmosphere	Proximate analysis				Ultimate analysis			
	M	A	FC	V	C	H	N	S_t
CG	3.23	9.62	83.2	3.98	85.0	0.26	0.67	0.16
N_2	1.10	7.28	86.9	4.71	86.4	1.16	1.02	0.32

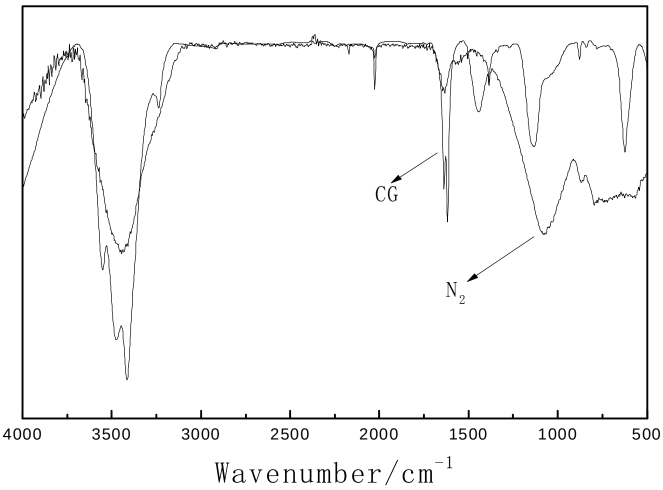
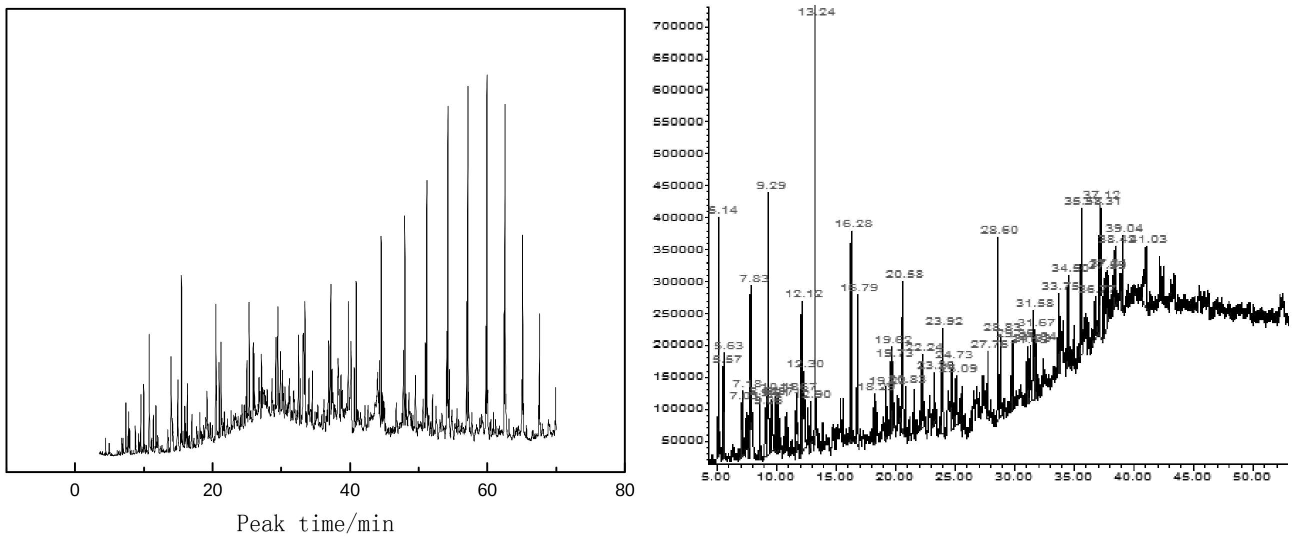


Figure 3. FTIR spectra of the bluecoke obtained under CG and N_2 atmosphere

Analysis of the tar

Gas chromatography-mass spectrometry (GC-MS) data of tar obtained under CG and N_2 atmosphere are shown
in Fig. 4. 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 CG and N_2 atmosphere are given in Table 4.



(CG) (N2)

Figure 4. GC-MS chromatograms of the tar obtained under CG and N_2 atmosphere

Table 4. Main components content of the tar obtained under CG and N_2 atmosphere (wt.%)

Atmos-phere	Alkanes	Olefins	Aromatic hydrocar-bons	Oxygen-containing functional groups
CG	45.2	3.40	9.70	17.9
N_2	32.2	7.50	44.2	8.90

It can be seen in table 4 that the alkanes compound content in tar obtained under CG atmosphere was up to 40.3 wt.%. Whereas the aromatic hydrocarbons compound content was just 6.80 wt.%. The alkanes compound content in tar obtained under CG atmosphere was 8.10 wt.% higher than that under N_2 atmosphere, meanwhile, the aromatic hydrocarbons compound content was 37.4 wt.% lower than that under N_2 atmosphere. It suggests that CG is more conducive to the formation of light component in coal tar during the coal pyrolysis.

CONCLUSIONS

(1) Compared with N_2 atmosphere, the yield of liquid products (tar and pyrolysis water) obtained under CG atmosphere increased by 8.0 wt.%, whereas the bluecoke yield decreased by 4.4 wt.%.
(2) Compared with N_2 atmosphere, the content of S element in the bluecoke obtained under CG atmosphere was 0.16 wt.% to meet Bluecoke Standard S-1 Grade, and the N element content was just 0.67 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 CG atmosphere was 8.10 wt.% higher than that under N_2 atmosphere, meanwhile, the aromatic hydrocarbons compound content was 37.4 wt.% lower than that under N_2 atmosphere.

ACKNOWLEDGMENT

This project was financially supported by the Scientific
Research Program of Shaanxi Provincial Education Department (no. 12JK0583), the Shaanxi Provincial Balanced-planning Science and Innovation Engineering Program of China (no. 2011KTDZ01-05-04) and the Yulin Planning Project of Science and Technology.

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