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SPECTROSCOPIC ANALYSIS OF PRODUCTS FROM LOW-RANK COAL MICROWAVE PYROLYSIS: EFFECT OF REACTION ATMOSPHERE [**]

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The pyrolysis of low-rank coal is considered as the optimal method of realizing clean and efficient production of blue coke, tar, and gas. The experiments of low-rank coal microwave pyrolysis under CO_2, CH_4, H_2, and circulating gas (CG) are studied in a custom-designed microwave oven to clearly clarify the effects of reaction atmospheres on pyrolysis temperature, products yields, and spectroscopic characteristics of pyrolysis products by the analysis techniques of FT-IR and GC-MS. The results show that among four pyrolysis atmospheres, the temperature-rise rate and final pyrolysis temperature under H_2 atmosphere are both highest, taking only 5.6 min to arrive at 750 ℃, and the final temperature is greater than 950 ℃. The liquid yields under CO_2, CH_4, H_2, and CG atmospheres are 21.8, 24.4, 28.2, and 26.8 wt.%, respectively. The contents of –OH, aromatic ring C=C double bond, and –C=O in the solid product under CH_4 atmosphere are highest, possibly because of the thermal polycondensation and the secondary degassing of the solid product. The hydrogenation of H free radicals dissociated from "rich hydrogen" gas results in an improvement in the alkane content and a decrease in the aromatic hydrocarbon content in tar, which is confirmed by the change in oxygen content in the solid product. The hydrogenation technique of circulating coal gas on low-rank coal microwave pyrolysis is economical, energy-efficient, and feasible, which is helpful in the development of coal processing technologies.

Keywords: *microwave pyrolysis, reaction atmosphere, spectroscopic analysis, tar, low-rank coal.*

СПЕКТРОСКОПИЧЕСКИЙ АНАЛИЗ ПРОДУКТОВ МИКРОВОЛНОВОГО ПИРОЛИЗА НИЗКОСОРТНЫХ УГЛЕЙ: ВЛИЯНИЕ РЕАКЦИОННОЙ АТМОСФЕРЫ

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Для изучения влияния реакционных атмосфер на температуру пиролиза, выход продуктов и спектроскопические характеристики продуктов пиролиза проведены эксперименты по микроволновому пиролизу низкосортных углей в атмосферах CO_2, CH_4, H_2 и циркуляционного газа (CG) в специ-

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ально разработанной микроволновой печи. Последние проанализированы методами ИК-Фурье-спектроскопии и газовой хроматографии-масс-спектрометрии. Скорость нарастания температуры и конечная температура пиролиза в атмосфере H_2 *самые высокие среди четырех атмосфер: для достижения температуры 750°C требуется всего 5.6 мин, конечная температура >950°C. Выход жидкости в атмосферах* CO_2, CH_4, H_2 *и CG составляет 21.8, 24.4, 28.2 и 26.8 мас.% соответственно. Содержание –OH, ароматического кольца с двойной связью C=C и –C=O в твердом продукте в атмосфере* CH_4 *является самым высоким, возможно, из-за термической поликонденсации и вторичной дегазации твердого продукта. Гидрирование свободных радикалов H, диссоциированных из "обогащенного водородом" газа, приводит к повышению содержания алканов и снижению содержания ароматических углеводородов в битуме, что подтверждается изменением содержания кислорода в твердом продукте. Метод гидрогенизации циркуляционного угольного газа при микроволновом пиролизе низкосортных углей экономичен и энергоэффективен, его использование способствует развитию технологий переработки угля.*

Ключевые слова: *микроволновый пиролиз, реакционная атмосфера, спектроскопический анализ, битум, низкосортный уголь.*

Introduction. With the development of electromagnetic theory and technology, microwave technology is not only applied in industrial production and daily life but also widely used in multidisciplinary fields of studies [1–4]. Among these researches, microwave technology-assisted thermal decomposition of solid fossil fuels is concerned especially with coal, which improves the temperature-rising rate of the pyrolysis reaction to enhance the pyrolysis efficiency, including improvement of yield and quality of tar and coal gas [5]. It is necessary for China to develop coal microwave pyrolysis technology, which is one of the advanced methods of coal treatment. Not all types of coal are suitable for pyrolysis; only low-rank coal that are rich in organic matter can benefit from pyrolysis. According to the BP statistical review of world energy [6], the total proven coal reserves of China comprise 138.819 billion tons at the end of 2017, and more than 55% of the coal reserves is low-rank coal. The other question refers to energy safety. The crude oil dependency of China has already broken through 70% in 2018 [7], which is a challenge for energy safety. As we discussed above, the yield and quality of coal tar can be improved by coal microwave pyrolysis technology, and if the coal tar can be partially instead of crude oil, this problem will be solved in time.

Numerous researches have shown that the yields and composition of pyrolysis products are strongly affected by the microwave pyrolysis conditions such as pyrolysis terminal temperature, heating rate, pressure, atmosphere, particle size, catalyst, coal, and reactor type [8–11]. In order to improve the yield and quality of tar, the optimized pyrolysis conditions and the effect mechanisms should be clearly studied. The pyrolysis atmosphere is one of the important pyrolysis conditions, which can change the reaction kinetics or take part in the pyrolysis reaction [12]. As for the solid product, the chemical and physical properties, pyrolysis, and combustion performance can be affected by the pyrolysis atmosphere [13–15]. Xu et al. investigated the effects of pyrolysis gas atmosphere on torrefied char, which are produced by camellia shell. They found that synergy effects of compositions in the pyrolysis gas improve the volatile matter content and heat value of the torrefied char and also promote the degradation of cellulose and hemicellulose when compared to the results of pyrolysis in an atmosphere of N_2 [16]. Tar, the most valuable product in the pyrolysis process, is always of particular concern, especially the effects of atmospheric pyrolysis on the yield and quality of tar [17, 18]. Prof. Hu`s research group analyzed the volatile fractions of coal tar under N_2, H_2, CH_4, and CO_2 atmospheres; they found that tar consists mainly of an alkyl substituent attached to the aromatic ring, which is produced by pyrolysis of Shendong coal at 750°C, and they believed that the increase in tar is caused by the free radical reaction [19]. Their group continued to study the effect of simulated coal gas on tar production. The results showed that an obvious improvement in tar yield was observed under a simulated coal gas atmosphere, and the aromaticity of tar decreased, which proved that free radicals, such as –H, $–CH_x$, were generated from coal pyrolysis under the simulated coal gas atmosphere, so that the yield and quality of tar were improved [20]. Zhang et al. also selected N_2, CO_2, CO, CH_4, and H_2 as carrier gas to investigate the atmosphere effects on product yields and quality of tar; they found that the highest yield of liquid product was obtained under a CH_4 atmosphere with the maximal yield of 58.7%, and the lowest yield of liquid product was 49.6% under a CO atmosphere. In addition, the methoxy-containing compounds in liquid product decreased, but the monofunctional phenols increased under CO and CO_2 atmospheres [21].

Although the effect of pyrolysis atmosphere on pyrolysis reaction has been largely researched, the related researches in the microwave pyrolysis field are few reported except for our previous researches. We found that low-rank coal microwave pyrolysis under a coal gas atmosphere can improve the yield and quality of tar when compared to conventional pyrolysis [22]. The yield of liquid product was 26.8% under optimal conditions of microwave power of 800 W, pyrolysis time of 40 min, coal particle of 5–10 mm, and a coal gas rate of 0.4 L/min [23]. However, the effects of the composition of coal gas on microwave pyrolysis reactions are unclear, and the synergic effect of each composition of coal gas is still unknow. It is necessary to clearly investigate how each pyrolysis atmosphere works on microwave pyrolysis products, especially the yield and quality of coal tar. This paper focuses on the effects of pyrolysis atmospheres of CO_2, CH_4, H_2, and circulating gas (CG) on coal microwave pyrolysis, including pyrolysis temperature, product yields, and the composition and structure of products. The research results will be helpful in popularizing low-rank coal microwave pyrolysis technology to realize clean conversion utilization of coal.

Experimental. *Coal sample*. Coal from Yulin coal field of China is selected because of its high potential hydrocarbon. The size of the coal particle is within 5–10 mm, which has proved beneficial for the precipitation of coal tar in our previous work. Details on the coal sample are known from the national standards of China (GB/T 30732-2014 and GB/T 31391-2015) and are shown in Table 1. The value of the molar ratio of carbon and hydrogen is 1.35, which is easy to calculate by the ultimate analysis.

TABLE 1. Proximate and Ultimate Analysis of Coal Sample (wt.% ad)

Proximate analysis				Ultimate analysis					n(C)/n(H)
M	A	FC	V	C	H	O_{diff}	N	S_t	
3.41	2.64	56.16	37.79	76.38	4.71	11.61	0.99	0.26	1.35

Note: ad stands for air dry basis; O_{diff} means the content of oxygen is calculated by difference; S_t is total sulfur in coal sample; n(C)/n(H) is molar ratio of carbon and hydrogen.

Apparatus and procedures. The pyrolysis apparatuses include four parts: microwave device, gas supply device, temperature detecting device, and products collector. As shown in Fig. 1, the microwave pyrolysis reactor is made of quartz, which has high microwave transmittance and is temperature resistant. A modified *K*-type thermocouple is employed to avoid ignition of the probe in the microwave field. The microwave pyrolysis system is connected by silicone and glass tubes, and the tube before the first-stage absorption cooler is wound by an electric tracing band to prevent the condensation of coal tar in the tubes. Fifty grams of coal sample is put in the microwave pyrolysis reactor, and the pyrolysis system is connected as in Fig. 1. Before beginning microwave pyrolysis, the air in the pyrolysis system is evacuated as much as possible. The microwave power, pyrolysis time, and gas flow rate are respectively set to 800 W, 40 min, and 0.4 L/min, which are the optimal conditions for low-rank microwave pyrolysis. The experimental apparatuses of the circulating gas are shown in our previous work [24].

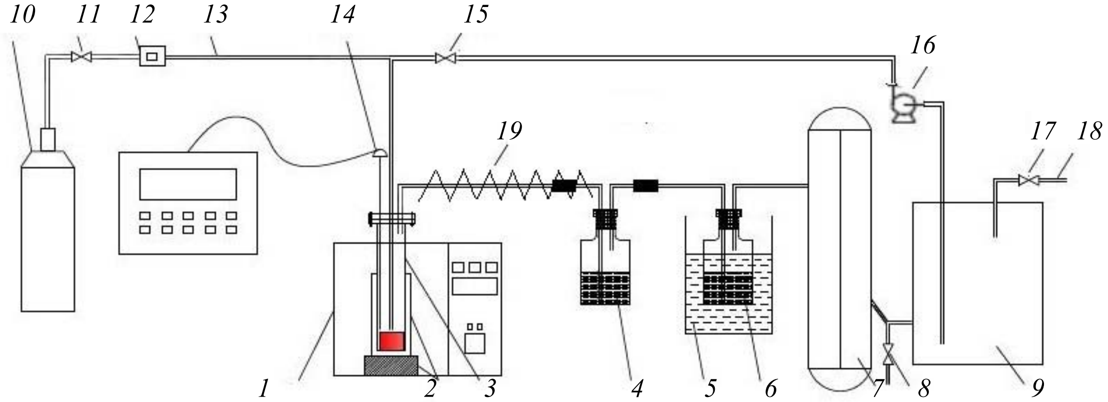

Fig. 1. Experimental apparatus of low-rank coal microwave pyrolysis under different atmospheres [24]: *1* — microwave device; *2* — ceramic insulation sleeve; *3* — quartz tube reactor; *4* — first-stage absorption cooler; *5* — circulating cooling liquid; *6* — second-stage absorption cooler; *7* — electrical tar precipitator; *8* — T-branch pipe and stop valve; *9* — gas collecting bag; *10* — mixed gas cylinder; *11* — stop valve; *12* — flowmeter; *13* — intake tube; *14* — thermocouple; *15* — stop valve; *16* — gas pump, *17* — stop valve; *18* — outlet pipe; *19* — electric tracing band.

Analysis of pyrolysis products. The masses of solid and liquid products are calculated from the difference of the masses of devices before and after the experiment. The yields of pyrolysis products are calculated via equations.

$$Y_{\text{solid}} = \frac{m_{1\,\text{after}} - m_{1\,\text{before}}}{m_0} \times 100\%, \tag{1}$$

$$Y_{\text{liquid}} = \frac{(m_2 + m_3 + m_4 + m_5)_{\text{after}} - (m_2 + m_3 + m_4 + m_5)_{\text{before}}}{m_0} \times 100\%, \tag{2}$$

$$Y_{\text{gas}} = 100\% - Y_{\text{solid}} - Y_{\text{liquid}}, \tag{3}$$

where Y_{solid}, Y_{liquid}, and Y_{gas} are the yields of solid, liquid, and gas products; m_0, m_1, m_2, m_3, m_4, and m_5 stand for the masses of coal sample, quartz tube reactor, first-stage absorption cooler, second-stage absorption cooler, electrical tar precipitator, and silicone tubes, respectively; the subscripts “after” and “before” refer to the stages after and before the pyrolysis experiments. The calculated data are the average of three repeated experimental results to reduce the experimental error.

Except for the analysis of pyrolysis temperature, product yield, and the proximate and ultimate analyses, FT-IR and GC-MS are employed to clearly clarify the effects of reaction atmospheres on the spectroscopic characteristics of the pyrolysis products (solid and liquid products) from low-rank coal microwave pyrolysis.

Results and discussion. *Pyrolysis temperature*. The pyrolysis temperatures of coal microwave pyrolysis under different atmospheres are shown in Fig. 2, which shows the difference in pyrolysis temperature focusing on the temperature-rise rate and final temperature. The whole microwave pyrolysis process can be roughly divided into two stages: fast and slow pyrolysis. It takes 5.6, 7.5, 10, and 13 min to arrive at 750°C under the H_2, CO_2, CG, and CH_4 atmosphere, respectively. Then the four temperature-rise rates slow down, and the pyrolysis temperatures tend to be stable and stay above 900°C. Coincidentally, the order of the final pyrolysis temperature from high to low in the four atmospheres is still H_2, CO_2, CG, and CH_4. The temperature-rise rate and final temperature of the H_2 atmosphere are the highest because hydrogenated reactions of coal are strongly exothermic. Compared to conventional pyrolysis, the high temperature-rise rate of microwave pyrolysis is obvious.

The pyrolysis temperature of coal is determined by microwave energy transfer and reaction heat. Here the effects of atmosphere on microwave energy transfer are insignificant because the mechanism of microwave energy transfer is electromagnetic polarization loss of coal, which results in an increase in the internal energy of the system. The interaction of microwave radiation with charge at the interface of metallic compositions in ash improves the temperature rise, forming a “hot-spot” in the microwave field [25–27]. Due to the similar composition of the coal sample, the microwave energy transfer of coal under different atmospheres is almost the same. However, the effects of atmosphere on reaction heat are obvious and involve multiple chemical reactions, such as hydrogenated reactions, reduction reactions, methanation reaction, and so on. The hydrogenation reactions of coal are exothermic ones, so that the pyrolysis temperature is active. The pyrolysis temperature under a CH_4 atmosphere is relatively low because of the energy consumption of CH_4 cracking in the microwave field [28].

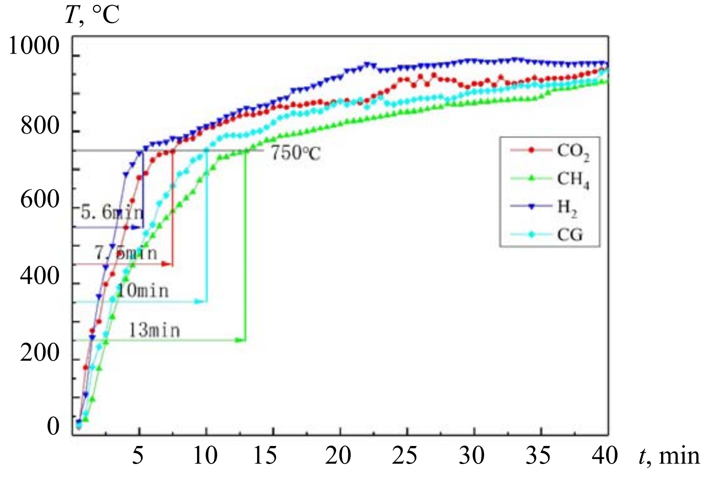

Fig. 2. Temperature-rise curves under different pyrolysis atmospheres.

Products yields. According to the calculated results of Eqs. (1)–(3), the yields of pyrolysis products under different pyrolysis atmospheres are shown in Fig. 3. The yields of solid product under CO_2, CH_4, H_2, and CG are 60.8, 61.2, 59.8, and 62.2 wt.%, respectively. The order of solid yield from large to small is CG, CH_4, CO_2, and H_2 atmosphere, which shows that coal pyrolysis under a H_2 atmosphere is more complete, resulting in a high yield of liquid or gas product. The liquid products including pyrolysis water and tar are obtained under CO_2, CH_4, H_2, and CG with yields of 21.8, 24.4, 28.2, and 26.8 wt.%. The order of liquid product from large to small is H_2, CG, CH_4, and CO_2 atmosphere, which indicates hydrogenated pyrolysis is beneficial for the formation of the liquid product, especially in a hydrogen-rich atmosphere. As shown in Eqs. (4) and (5)

$$CH_4 \rightarrow CH_x + H \tag{4}$$

$$H_2 \rightarrow 2H, \tag{5}$$

hydrogen-rich atmospheres, such as H_2, CH_4, and CG, can provide more free hydrogen in the microwave field, which effectively promotes the pyrolysis reactions of low-rank coal. The yields of gas product under CO_2, CH_4, H_2, and CG atmosphere are 17.4, 14.4, 12.0, and 11.0 wt.%, respectively. The order of gaseous product yield from large to small is CO_2, CH_4, H_2, and CG atmosphere, where the yield of gas product under CO_2 atmosphere is highest, reaching 17.4 wt.%. This is due to the gasification reaction of CO_2 and C resulting in an increase in the yield of gas product:

$$C + CO_2 \rightarrow 2CO \tag{6}$$

With respect to satisfying the final pyrolysis temperature, hydrogen free radicals may play the key role in changing the product distribution, so that (I) the macromolecular aromatic group structure is fully cracked, (II) the primary volatiles rapidly escape from the coal and decrease the secondary reaction, and (III) the coal pyrolysis reaction is dominant compared to the secondary cracking reaction of tar. The gas activity of CH_4, H_2, and CG increased as it is influenced by the catalytic effect of inorganic minerals in coal and microwave radiation [22]. Methyl or methylene CH_x groups, H free radicals dissociated from CH_4, H_2, and CG gas, and micromolecular free radicals from the fracture of the macromolecular structure bridge bond in coal rearrange to generate tar [29–31], inhibiting the polymerization of free radicals and the secondary reaction involving tar, thus improving the tar yield [32].

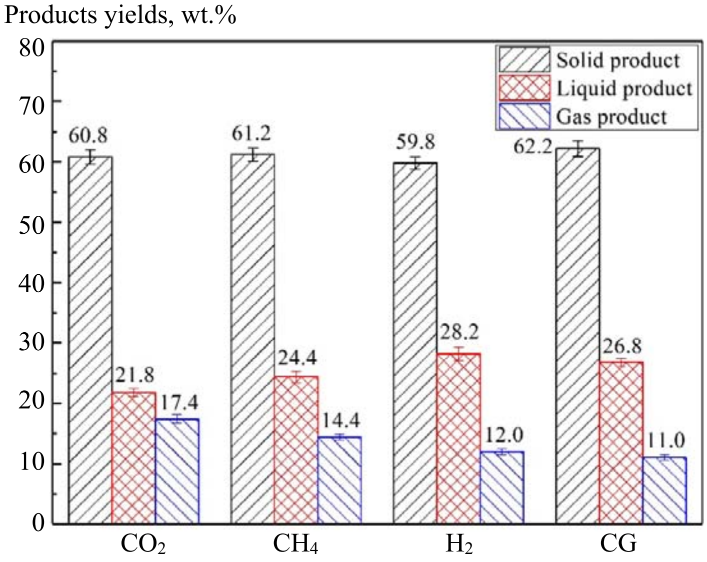

Fig. 3. Products yields under different pyrolysis atmospheres.

Products characteristics. Solid product. The proximate and ultimate analyses of the solid product under different pyrolysis atmospheres are shown in Table 2. Compared with the data of raw coal, the volatile and H element content of the solid product decreased obviously, while ash, fixed carbon, and C element content increased significantly. The increase in ash is due to the volatilization of organic matter during coal pyrolysis, which leads to mineral enrichment.

As the pyrolysis temperature rises, more aliphatic carbons are released into the gas phase because of the escape of primary volatiles, whereas aromatic carbons are fixed onto condensed aromatic rings. Further, the aromatization degree of the solid product intensifies, resulting in a corresponding increase in elemental C and fixed carbon. Therefore, coal pyrolysis essentially is a process of dehydrogenation, deoxygenation, and carbon enrichment. Compared with a CO_2 atmosphere, the contents of S, N, and O elements in the solid products under a “hydrogen-rich” atmosphere are relatively lower, which can be explained by the fact that H free radicals dissociated from CH_4, H_2, and CG gas in a microwave field may combine with the functional groups of N, S, and O, and the heteroatom in the raw coal structure usually enters in tar or coal gas with the volatile; thus sulfur-fixation, nitrogen-fixation, and oxygen-fixation reactions are effectively inhibited. According to the blue coke standard of China [33], the sulfur content in the solid product under CH_4, H_2, and CG atmospheres are less than 0.30 wt.%, which meets the S-1 grade of blue coke standard, and the fixed carbon content ranges from 83.2 to 85.2 wt.% to meet the FC-4 grade of blue coke standard.

TABLE 2. Proximate and Ultimate Analyses of Solid Products under Different Pyrolysis Atmospheres (wt.%, rad)

Atmosphere	Proximate analysis				Ultimate analysis				
	M	A	FC	V	C	H	N	S_t	O_{diff}
CO_2	3.98	7.06	84.1	4.86	82.6	1.57	1.00	0.35	3.44
CH_4	3.25	7.13	85.2	4.42	85.6	0.89	0.88	0.29	1.96
H_2	2.84	8.12	84.9	4.14	86.0	0.47	0.48	0.24	1.85
CG	3.23	8.62	84.2	3.95	86.0	0.26	0.67	0.16	1.06

Note: proximate and ultimate analyses of solid product are based on the national standards of China; abbreviation M, A, FC, and V are defined according to the national standards of China [34, 35].

The FTIR spectra of the solid product under different pyrolysis atmospheres are shown in Fig. 4. Although the position of characteristic peaks of the solid product in the FTIR spectra are basically the same, there are larger differences in the strength of the peak and peak area, which suggests that the contents of functional groups in the solid product are different from each other. According to the standard FTIR spectra library, the peak at 3400 cm^{-1} is ascribed to the stretching vibration of –OH or –NH functional groups associated with the hydrogen bond, but the nitrogen content of low-rank coal is very low; therefore, –NH functional groups have little influence. The content of –OH functional groups may be high because of the strongest peak position transformation. The peak at 1600 cm^{-1} is attributed to the stretching vibrations of the aromatic ring C=C double bond and –C=O associated with the hydrogen bond. The contents of the above functional groups are the highest under a CH_4 atmosphere, possibly because of the thermal polycondensation and the secondary degassing of the solid product, where CH_x groups dissociate from CH_4. On the one hand,

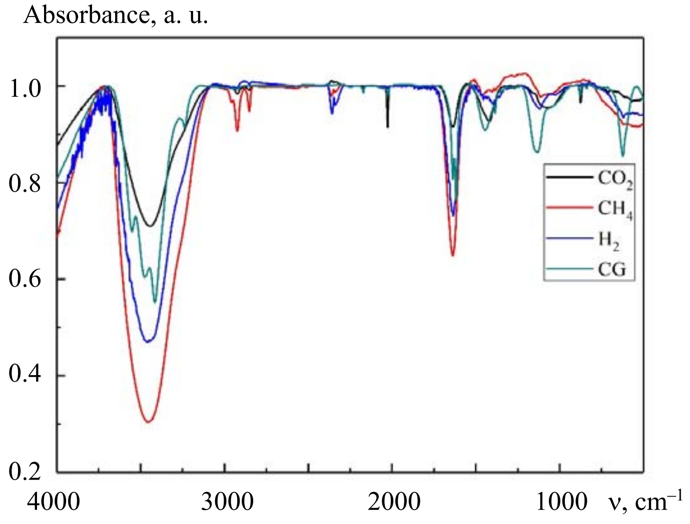

Fig. 4. FTIR spectra of solid product under different pyrolysis atmospheres.

combined small free radical molecules derived from the coal pyrolysis process turn into escaping gaseous hydrocarbon volatiles. On the other hand, connecting on the bridge bond of aromatic-structure units results in deepening of the polycondensation degree of the solid product, increase in the aromatic nucleus, improvement in the spatial structure arrangement of the solid product, and enhancement of the intermolecular interaction force, which inhibits carbonyl and phenolic hydroxyl. The ether bond in the aromatic structure from cracking into CO and aromatic-ring polycondensation dehydrogenation combines with –OH to turn into pyrolysis water at the late stage of coal pyrolysis [36]. The wavenumbers of the FTIR spectra below 1000 cm^{-1} are close to the fingerprint region. The infrared spectral lines are in disorder, and no regularity can be seen because inorganic minerals have a larger influence in coal.

Liquid product. Gas chromatography-mass spectrometry (GC-MS) data of tar under different pyrolysis atmospheres are shown in Fig. 5. The GC-MS chromatograms show many chromatographic peaks without a single component of the individual chromatographic peak, which shows that coal tar is a complex mixture composed of a variety of organic compounds. Based on GC-MS analysis, the main components of tar under different pyrolysis atmospheres are listed in Table 3. No matter the reaction atmosphere, the content of alkanes is the highest in tar, and even the contents of alkanes under CH_4, H_2, and CG atmospheres are greater than 40%. The order of olefin content from high to low is CO_2, CH_4, H_2, and CG, which shows that the combined contents of alkanes in a reduced atmosphere are good for improving molecular saturation. The contents of aromatic hydrocarbons under reduced atmospheres are both lower than that under a CO_2 atmosphere, which also shows that the hydrogenation of H free radical will decrease the content of aromatic hydrocarbons because benzene series are converted into cycloalkanes or broken into straight-chain hydrocarbon. However, the contents of phenols are basically similar, which are both at about 17%. This result indicates that the hydroxyl in phenol is very stable, which needs energy and catalyst in hydrodeoxygenation [37] and is not easily reduced by H free radical. The H free radicals dissociated from CH_4, H_2, and CG gas reacts with aliphatic hydrocarbons at high temperature, resulting in its connecting to the side chain of the aromatic ring and cracking into straight-chain hydrocarbon molecules to avoid the second cleavage and cross-linking of free radical during pyrolysis [38].

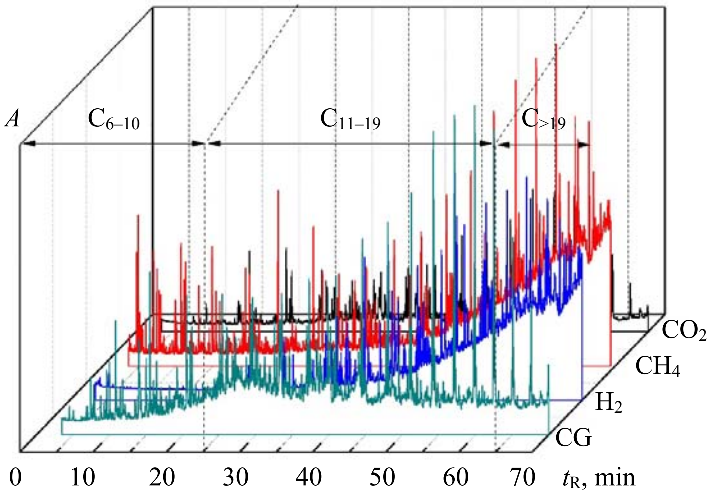

Fig. 5. GC-MS chromatograms of tar under different pyrolysis atmospheres.

TABLE 3. Main Composition of Tar under Different Pyrolysis Atmospheres (wt.%)

Atmosphere	Alkanes	Olefins	Aromatic hydrocarbons	Phenols
CO_2	35.5	8.30	12.0	17.2
CH_4	41.8	5.3	8.50	17.8
H_2	45.2	3.40	9.70	17.9
CG	40.3	2.70	6.80	17.4

Based on the composition analysis characterization of the solid and liquid products from different pyrolysis atmospheres and considering both liquid product yields and component contents of coal tar, the best reaction atmosphere for the microwave copyrolysis processing of low-rank coal is H_2, followed by circulating gas, CH_4, and CO_2. Tar yields under H_2 and CG are nearly equal, but the alkane content of tar under the H_2 atmosphere is higher than that under a CG atmosphere. H_2 and CG can realize coal hydrocracking, increase tar yield, and increase the alkane content in tar. In terms of economy and comprehensive utilization of resources, realizing microwave pyrolysis technology under a coal gas atmosphere by introducing part coal gas of the microwave pyrolysis products circularly into the pyrolysis system is economical, energy-efficient, and feasible.

Conclusions. The effects of reaction atmospheres on yields and characteristics of pyrolysis products are obvious: The coal microwave pyrolysis reactions under different atmospheres both show high temperature-rise rates and high final pyrolysis temperatures, especially in a H_2 atmosphere. The order of liquid product yield from high to low is H_2, CG, CH_4, and CO_2, and the highest yield of liquid product reaches 28.2% under a H_2 atmosphere; Sulfur-fixation, nitrogen-fixation, and oxygen-fixation reactions are effectively inhibited under a “hydrogen-rich” atmospheres; also, a “hydrogen-rich” atmosphere improves the alkane content and decreases the aromatic hydrocarbon content in tar; this is due to the H free radicals dissociated from CH_4, H_2, and CG gas reacting with aliphatic hydrocarbons at the high temperature, resulting in the generation of cycloalkanes or breaking the straight chains of hydrocarbons during pyrolysis; however, the phenol content is unaffected by the atmosphere. Circulating coal gas employed as the reaction atmosphere in low-rank coal microwave pyrolysis technology is economical, energy-efficient, and feasible.

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