Study on pyrolysis gas in thermal extraction of Bai Yinhua lignite with industrial washing oil

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Abstract. Industrial washing oil as solvent, pyrolysis gas produced from Bai Yinhua lignite during thermal extraction was studied by gas chromatography. The effects of temperature and solvent coal ration on coal pyrolysis gas were investigated. The results showed that: Pyrolysis gas produced mainly in CO, CO_2, O_2, H_2, CH_4, and so on, in which the total amount of oxygen containing compounds nearly 40%, significant effects of deoxidation was achieved. The increase of heat extraction temperature can significantly increase the degree of bond breaking and the gas formation rate, the gas yield and the rate of oxygen increase significantly, while the gas yield increases with the decrease of the solvent coal ration.

1. Introduction

China is rich in lignite resources, the reserves of which account for more than 13% of proven coal. Among them, the lignite reserves in the northeast of Inner Mongolia accounts for about 3/4. The southwest region is mainly dominated by Yunnan, which makes up about 1/5. Northeast, east and south-central region is about 5% [1-2]. Lignite is the lowest degree of metamorphism of coal, the degree of coalification between peat and bituminous coal. Lignite has the disadvantages of high inherent moisture content, high volatile, easy to self ignition and low heat [2-4]. Without any bond performance, most of the lignite is used for combustion to heat, so it cannot be directly used for coking. Super clean coal can be extracted from lignite by using solvent thermal extraction technology [5-6]. Because Super clean coal has strong bonding property, it can be used as a high-quality binder for coking coal blending which can achieve the purpose of expanding coking coal resources [7-8].

Coal-derived oils have similar structural properties with coal. Their thermo chemical properties are stable, and their sources are reliable, easy to recycle, and have good economy. Cui *et al* [6] reported that the extraction yield was 66.8% for Xiao-kang village 1/3 coking coal using thermal extraction technology with industrial washing oil at 380 ^{o}C. The recycling of industrial washing oil was studied. It shows that industry washing oil has the excellent extraction performance, and it is a preferred solvent for thermal extraction of coal.

In the process of thermal extraction, the organic matter with high activity in coal is extracted, ash is retained in the residue. During thermal extraction, the break of bonds in the coal molecular structure is accompanied with the pyrolysis of coal and gas was generation. Because of the presence of solvent, the gas produced in the pyrolysis process and the high temperature pyrolysis of the coal alone are different during thermal extraction. It reflects the change of coal molecular structure in a certain extent

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during thermal extraction. In addition, thermal extraction process is accompanied by reduction, condensation, hydrogenation reaction, which requires a qualitative and quantitative study on the pyrolysis gas [9].

With the popularization and development of gas chromatography technology, it possible to study the complex composition of gases produced in the process of thermal extraction. Either qualitative research or quantitative research will be better than the traditional methods. In this paper, pyrolysis gas produced from Bai Yinhua lignite during thermal extraction with wash oil as solvent will be studied by gas chromatography.

2. Experiment

2.1 Coal samples

In the experiments coal samples were used of the Inner Mongolia Bai Yinhua lignite. The sample preparation was according to the National Standard GB474 - 1996. They were crushed and divided less than 100 μm in 150min at 100 ºC in drying and vacuum conditions. The coal samples were stored in a dryer, which were low temperature and avoiding light. Industrial analysis and elemental analysis data of coal was shown in table 1. The main functional groups of active components in Bai Yinhua lignite was shown in table 2.

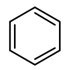
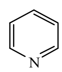
Table 1. Proximate and ultimate analysis of samples.

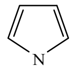
	Proximate analysis / %[1]			Ultimate analysis / % [1], ad			
Mad	Aad	Vad	C	H	O[2]	N	S
16.29	14.61	36.42	52.98	4.06	41.44	0.99	0.53

[1]Percent of weight

[2]By defferent

Table 2. Main functional groups of active components in Bai Yinhua lignite.

Group		Structural formula
Core structure	Aliphatic hydrocarbon chain	—C—C— —C=C—
	Aromatic nucleu	
Oxygen group	Hydroxyl group	—OH
	Carboxyl group	—COOH
	Methoxyl group	—OC
	Carbonyl group	C=O
Alkyl side chain	Methyl side chain	—C
	Ethyl side chain	—C—C
	Propyl side chain	—C—C—C
Nitrogen groups	Pyridine	

Pyrrole 

2.2 Experimental method

The experiments were carried out in a thermal extraction device which was designed by ourselves. A certain size of Baiyinhua lignite was added in an autoclave after full mixing with the industry washing oil. The coal was extracted at a certain temperature in N_2 atmosphere after staying for 10 min. After the extraction, when the reaction system was cooled to room temperature, The qualitative and quantitative analysis were carried out by gas chromatography.

2.3 Analysis method

Using GC-9790 gas chromatograph. The gas chromatograph was producted by Wenling Analytical Instrument Co. Ltd. Operating conditions:

- Carrier gas: Argon, 5A molecular sieve packed column;
- Carrier gas: Hydrogen, GDX-103 packed column.
- Column temperature: 50 ºC;
- Gasification room temperature: 70℃;
- Detector temperature: 180 ºC;
- Sample volume: 1 ml.

Standard gas was choosed by the known gas mixture componets which was producted by the Dalian Special Gas Co. Ltd, Qualitative analysis with retention time, quantified by an external standard method.

3. Results and discussions

3.1 Analysis of main gas composition and content

The gas content after extraction was shown in figure 1, which was at the condition of the solvent and the coal 10:1; the extraction temperature is 380 ºC. It was shown that CO_2 and N_2 content were highest; CH_4, CO and C_2H_6 were low; H_2, O_2 and C_2H_4 were lowest. N_2 content is higher because the whole process of heat extraction was carried out in the N_2 atmosphere, so the reaction of the mixed gas, N_2 also occupies a considerable part of the content. The total amount of oxygen-containing compounds in the figure was nearly 40%, indicating that the oxygen removal effect of solvent extraction of Baiyinhua lignite was significant. In addition, the content of organic hydrocarbon gas is relatively large such as CH_4, this was because the thermal extraction temperature exceeds the thermal decomposition temperature of coal, which will lead to functional groups and carbon chain rupture. Figure 2 shows main ways to generate methane during Thermal Extraction.

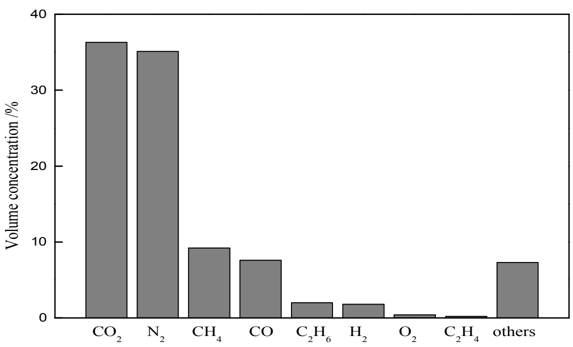


Figure 1. Distribution of gas content

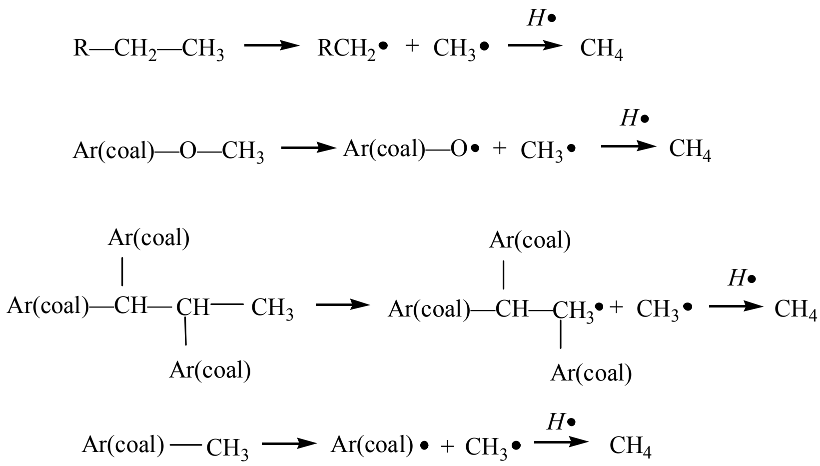


Figure 2. Main ways to generate methane during thermal extraction

3.2 Effect of temperature on pyrolysis gas

The effect of temperature on pyrolysis gas was investigated under the condition of the solvent and the coal 10:1. The change of gas yield with temperature was shown in figure 3. It can be seen that the gas yield increases with the increase of temperature. When the temperature was lower than 300 ^{o}C, the increase of gas yield was relatively slow, when the temperature reaches 300 ℃, the gas production rate increased rapidly, reaching 4.9% at 400 ^{o}C.

According to the theory of modern coal chemistry, coal was a complex macromolecular compound, it was composed of a three-dimensional cross-linked space network [10] These aromatic and hydrogenated aromatic structures were connected by methylene or longer aliphatic hydrocarbon chains. The periphery of the basic structure was connected with an alkyl side chain and a variety of functional groups. Alkyl side chain mainly has $-CH_2$-, $-CH_2$-CH_2- , the functional group mainly contains oxygen functional group, including phenolic hydroxyl group, carboxyl group, carbonyl group, carbonyl group and so on[11]. Figure 4 was a schematic diagram of two-phase model. The network structure of coal was demonstrated by the two-phase model.In the process of thermal extraction, with the increase of temperature, the side chains and functional groups in the coal molecules increased, the chain of the alkyl side chain would generate methane and other hydrocarbon gases. The fracture of the oxygen containing functional groups would generate CO, CO_2 and other gases. Small aromatic polycyclic aromatic molecules dissolved in the solvent. The bond breaking degree of coal molecules and the gas yield increased significantly when increasing temperature at the extraction temperature exceeding 300 ^{o}C [12].

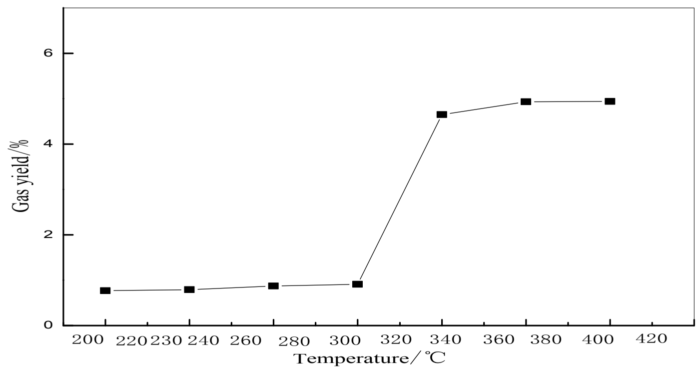


Figure 3. Change of gas yield with temperature

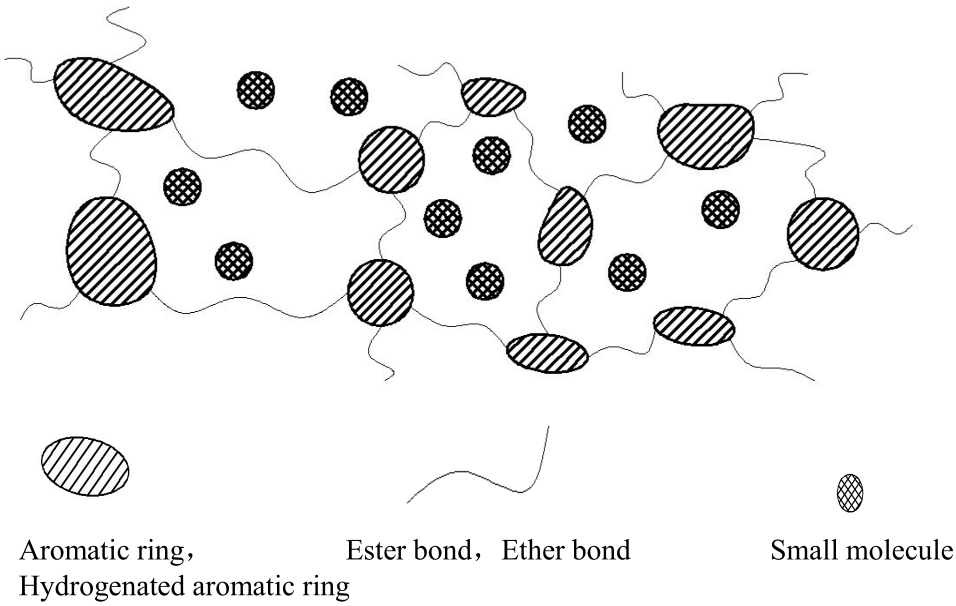


Figure 4. Schematic diagram of Two-phase model

The change of deoxidation rate with temperature was shown in figure 5. Before 300 °C the deoxidation rate increased unobviously with the increase of extraction temperature, After 300℃ the rapid increase to 340 °C deoxidation rate reached 7.1%, continue to heat up the deoxidation rate changed slowly. The removal of oxygen element in coal mainly due to the weak oxygen bond, which was easily broken by the thermal effect, and the CO and CO_2 gas could be formed quickly. The oxygen bond broken more because of temperature rising. When the temperature reached a certain degree, the deoxidation rate increased rapidly. At last the weak oxygen bond rupture was basically completed, the deoxidation rate did not increase.

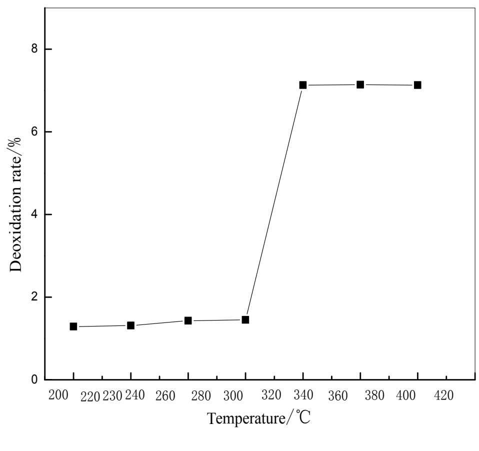


Figure 5. Change of deoxidation rate with temperature

3.3 Effect of the ratio of solvent to coal on pyrolysis gas

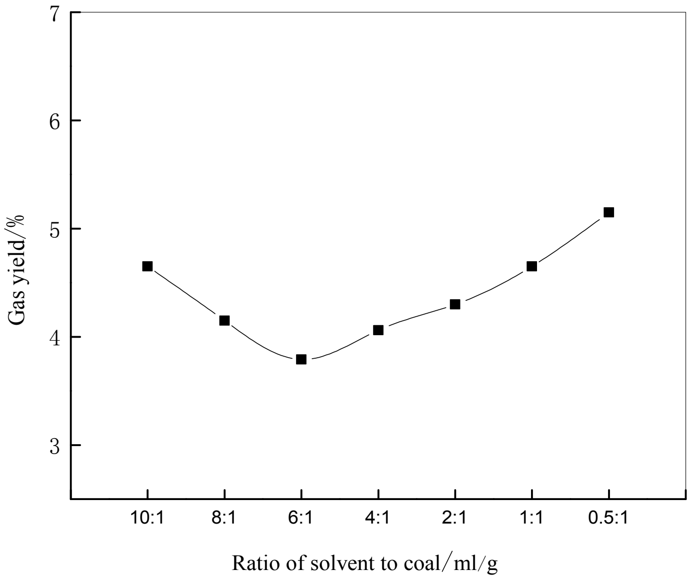


Figure 6. Effect of the ratio of solvent to coal on the pyrolysis gas

The effect of the ratio of solvent to coal on the pyrolysis gas was investigated at 380 ^oC. Figure 6 shown the change of gas yield with the ratio of solvent to coal. It was shown that the gas yield decreased firstly and then increased with the decrease of the ratio of coal to gas, which reached a turning point when the ratio of solvent to coal was 6:1. The results shown that the ratio of solvent to coal has a great influence on the formation of gas. The solvent can penetrate and swell the coal, which was helpful to the fracture of the bond in the coal, and the smaller molecular free radicals were generated, and the gas was produced by hydrogenation and condensation. Therefore, the larger soluble coal ratio was favorable for the formation of gas. But with the ratio of solvent to coal continued to decrease, the lack of adequate organic solvent components dissolved in the coal, the organic components of pyrolysis reaction under high temperature and gas generation. So with the further decrease of the ratio of coal to gas, the gas yield increased gradually.

4. Conclusion

- During the thermal extraction of Bai Yinhua lignite, the gas produced by pyrolysis mainly include CO, CO_2, O_2, H_2, CH_4, C_2H_4, C_2H_6, etc.. The total amount of oxygen-containing compound was nearly 40%, It indicated that the oxygen element removal of Baiyinhua lignite was significant by thermal extraction.
- The degree of bond breaking and the gas formation rate can significantly accelerated by increasing temperature. The effect of deoxidation rate tended to be gentle when the temperature touched 340 ^oC.
- The effect of the ratio of solvent to coal on the pyrolysis gas was significant, With the decrease of the ratio of solvent to coal, the number of small molecular organic residue increased, it was easier to form pyrolysis gases when no solvent protected at high temperature.

Acknowledgements

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