

Composition and structure characteristics and pyrolysis products distribution of light residue from Yinggema lignite

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December 18, 2022

Abstract

Yinggema lignite (YL) was extracted with isometric acetone/carbon disulfide mixed solvent at room temperature under ultrasonication to remove the soluble organic matter and obtain the extract residue (RYL), and then RYL was separated by density difference with carbon tetrachloride under ultrasonication to obtain the light residue (LRYL). Composition and structure characteristics and pyrolysis products distribution of YL and LRYL were analyzed by Thermogravimetry-Fourier transform infrared spectrometer-Gas chromatography/mass spectrometer (TG-FTIR-GC/MS).

Composition and structure characteristics and pyrolysis products distribution of the light residue from Yinggema lignite

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Abstract: Yinggema lignite (YL) was extracted with isometric acetone/carbon disulfide mixed solvent at room temperature under ultrasonication to remove the soluble organic matter and obtain the extract residue (R_{YL}), and then R_{YL} was separated by density difference with carbon tetrachloride under ultrasonication to obtain the light residue (LR_{YL}). Composition and structure characteristics and pyrolysis products distribution of YL and LR_{YL} were analyzed by Thermogravimetry-Fourier transform infrared spectrometer-Gas chromatography/mass spectrometer (TG-FTIR-GC/MS). Results show that the extraction-stratification treatment could dissolve small molecular compounds in the coal and some of the intermolecular forces were disrupted, leading to the reduction of resistance for volatile fraction escaping from the coal, and thus increasing the pyrolysis reactivity. C=O absorption peak area and intensity of LR_{YL} were significantly reduced, presumably due to the high hydrogen donating ability of acetone, destroying the C=O functional group in YL. Mass loss and the maximum mass loss rate peak temperature of YL and LR_{YL} are little different, indicating that the macromolecular network structure of the coal was not destroyed, while LR_{YL} showed a

significant mass loss rate peak at 210°C, speculating that the extraction-stratification treatment dissolved some of the small molecular compounds in the coal and eluted some of the minerals in the YL, resulting in the structure of the coal becoming loose, and the pyrolysis temperature of some of the organic matter in the coal shifting towards lower temperature region. TG-FTIR test showed that the main gaseous products of the pyrolysis of both samples are H₂O, CH₄, CO₂ and CO, with a small amount of NH₃. Hydrocarbons detected by GC/MS in the pyrolysis products of YL and LR_{YL} at 450 °C were mainly alkanes, alkenes and arenes, with the higher relative contents of alkanes of 31.1% and 36.2%, followed by arenes of 27.1% and 22.6%, respectively. The oxygen-containing compounds were mainly alcohols and phenols, with a small difference in the relative content of alcohols, while a larger difference in the relative content of phenols of 17.6% and 22.1%, respectively, can be observed, speculating that the extraction-stratification treatment could expose more oxygen-containing functional groups and bridge bonds, facilitating their conversion to phenolic hydroxyl groups during pyrolysis process, resulting in more phenolic compounds being produced.

Keywords: Lignite; Light residue; Pyrolysis; Products distribution; TG-FTIR-GC/MS

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1. Introduction

Lignite consists of a number of similar but not identical molecular structure that are highly cross-linked in three dimensions - a network of "basic structure unit", mainly benzene rings and naphthalene rings connected by bridge bonds such as methylene, ether, methylene ether and thioether bonds [1-4]. There are also a number of small molecular compounds in coal, mostly derived from the original components of coal-forming plants and low molecular polymers formed during coal formation, which are mainly associated with the macromolecules in coal by non-covalent bonds, such as hydrogen bonds, van der Waals forces and π - π interactions, and dispersed in the macromolecular network structure of coal. Usually, by non-destructive means such as solvent extraction, the non-covalent bonds and weak covalent bonds present in coal can be weakened [5-8]. Therefore, the residue after solvent extraction more closely resembles the macromolecular network structure of the coal.

Solvent extraction is one of the most common methods used to study the composition and structure of coal. Solvent extraction process is often complex, which is not only related to the structure of the coal, but is influenced by the properties of the solvent. In the extraction process, the solvent firstly penetrates into the macromolecular network of the coal, weakening the intermolecular forces in the cross-linked network, then joins with the smaller soluble molecules, and finally diffuses out of the pore structure of the coal [9,10]. Various methods have been used to improve the extraction rate of coal, including physical methods such as ultrasonic radiation, microwave radiation and anti-colloid extraction, and chemical methods such as acid washing, hydrolysis and oxidation, which serve to improve the solvent extraction rate of coal by removing or breaking some interactions between coal structural units [11-16]. Iino et al. [17] extracted several raw coals with CS₂/NMP mixture solvent at room temperature, and results of the characterization of the raw coals, extracts and residues suggested that the chemical reaction between coal and solvent did not occur to a significant extent during the extraction. The increase of extraction rate and yield by the mixed solvent, compared with CS₂ and NMP alone, has been explained by the increase of solubility and diffusivity of the extracts in the mixed solvent, and swelling effect of the coals was also thought as an important factor. Norman et al. [18] investigated the extraction of Cretaceous bituminous coal by quinoline under ultrasonic radiation, with variations in ultrasonic intensity ranging from 0.455 W·cm⁻² to 1.46 W·cm⁻² and temperature ranging from 15-300 °C, and the results showed that at least 58% of the organic matter was mobile and could be extracted from the coal without destroying any chemical bonds. The average molecular weight of the extracts ranged from 340-1055. Numerous studies have indicated that there are more small molecule compounds in coal, trapped in a three-dimensional cross-linked structure, which can be removed by solvent extraction, and the treated samples provide a more comprehensive and realistic picture of the coal structure.

Pyrolysis is a complex free radical reaction involving the breaking and formation of chemical bonds, and the characteristics of the pyrolysis process are closely related to the macromolecular network structure of the coal.

Xie et al. [19] performed a semi-quantitative characterization of the chemical structure of six coal samples with different ranks by a series of original infrared structure parameters, and the pyrolysis reactivity of the samples were quantitatively characterized by a comprehensive devolatilization index. A correlation was established between the infrared structure parameters and pyrolysis reactivity. Results showed that the infrared structure parameters can effectively reveal the distribution characteristics of chemical bonds in coal, and a well positive correlation was established between the infrared structure parameter and the pyrolysis reactivity. Jiang et al. [20] investigated the chemical properties, pyrolysis behavior and pyrolysis product distribution of Shenmu coal by thermogravimetric analyzer coupled with fourier transform infrared spectroscopy (TG-FTIR) and pyrolyzer coupled with gas chromatography/mass spectrometry (Py-GC/MS). The main volatile species detected from TG-FTIR were CO₂, CO, CH₄, C₂H₄, aliphatic hydrocarbons, light arenes, compounds containing C=O bonds and containing C-O bonds. According to the fast pyrolysis results by Py-GC/MS, the volatile species could be divided into eleven species including alkenes, cycloalkenes, alkanes, cycloalkanes, arenes, phenols, ethers, ketones, alcohols, N-containing species, and other species. Pyrolysis is an important step in coal conversion technology and an effective method for hierarchical utilization of coal. A number of data related to pore structure, infrared structure parameters, pyrolysis reactivity and kinetic parameters can be combined to develop a new model for the devolatilization process, to speculate the pyrolysis mechanism and to predict the distribution of pyrolysis products, and thus providing a direction for optimizing the pyrolysis process.

In our group, light residue from Yinggema lignite was subjected to thermal dissolution with cyclohexane as the solvent at 160°C under 4 MPa [21]. However, the infrared characteristics, thermal behavior and pyrolysis products distribution of the light residue were not investigated. Therefore, based on the previous work, in this study, Yinggema lignite (YL) was extracted with isometric acetone/carbon disulfide mixed solvent at room temperature under ultrasonication to remove the soluble organic matter and obtain the extract residue (R_{YL}), and then R_{YL} was separated by density difference with carbon tetrachloride under ultrasonication to obtain the light residue (LR_{YL}). Composition and structure characteristics and pyrolysis products distribution of YL and LR_{YL} were analyzed by Thermogravimetry-Fourier transform infrared spectrometer-Gas chromatography/mass spectrometer (TG-FTIR-GC/MS).

2. Experimental

2.1. Material

The coal sample used for this experiment was collected from Yinggema coal mine in Xinjiang Uygur Autonomous Region, China, which is a typical low-rank coal. The sample was pulverized to pass through a 200-mesh sieve (<74 μm) followed by desiccation in a dryer at 105 °C for 12 h before use.

2.2. Preparation of LR_{YL}

As shown in Fig. 1, YL (10 g) was added to a conical flask with 200 mL isometric acetone/carbon disulfide mixed solvent (IMACDSMS) in it. Then, the conical flask was placed in an ultrasonic instrument at room temperature for 1.5 h. The mixture in the flask was filtered to obtain the extract liquid and extract residue (R_{YL}), and the above procedure was repeated until the extract liquid was nearly colorless.

R_{YL} was extracted with 200 mL carbon tetrachloride under the ultrasonication for 1 h, then the mixture was poured into a separatory funnel, standing for 0.5 h. Subsequently, layering appeared in the funnel, and the bottom precipitate (heavy residue) was removed out in this step. The upper mixture from separatory funnel was filtered, and the filter cake (light residue) was dried at 105 °C for 12 h to obtain LR_{YL}.

3. Results and discussion

3.1. Coal analysis

Table 1 showed the proximate and ultimate analyses of YL and LR_{YL}. According to the results of the proximate analysis, it can be seen that the moisture and ash contents of LR_{YL} are 6.75% and 6.53%, reduced by 4.63% and 37.75%, respectively, compared to YL, which might be attributed to that some of

the inorganic components or minerals in YL were removed by extraction-stratification treatment [22]. In addition, the volatile and fixed carbon yield of LR_{YL} were reduced by 37.75% and 28.86%, suggesting that the extraction-stratification treatment could cause the small molecules in the coal to be dissolved, and some intermolecular forces might be destroyed, leading to a reduction of volatile yield.

The results of ultimate analysis show that C element and H element contents of LR_{YL} decrease, while the content of O element increase significantly, indicating that some of the hydrocarbons in the coal were dissolute by the extraction-stratification treatment, while the macromolecular structure of the coal was not destroyed, and the main oxygen-containing functional groups and oxygen-containing bridge bonds were nearly not broken, resulting in a relative increase in the O element content.

3.2. FTIR analysis

As presented in Fig. 2, there is a large difference of absorption peaks at 2927 cm⁻¹, 1639 cm⁻¹, 1109 cm⁻¹ and 615 cm⁻¹ for LR_{YL} compared to YL. The peak around 3436 cm⁻¹ is belonged to the functional group of -OH. The increase in intensity of the absorption peaks of self-associated -OH and cyclic -OH in LR_{YL} suggests that the aromatic lamellae of LR_{YL} are more ordered, and the spatial arrangement of the macromolecule structure of which is tighter [23]. The absorption peaks observed at 2847 cm⁻¹ and 2927 cm⁻¹ are attributed to the asymmetric stretching vibrations of -CH₃ and -CH₂ in alkanes respectively, and the peak intensity of LR_{YL} is weaker compared to YL. The C=O absorption peak area and intensity at 1639 cm⁻¹ of LR_{YL} is significantly lower, presumably due to the strong hydrogen donating ability of acetone, which might destroy the C=O functional group in YL. The peak of stretching vibration of -Si-O in LR_{YL} is located at around 1109 cm⁻¹, and the intensity of the peak of LR_{YL} is stronger than that of YL, speculating that the substitution reaction, like Si-OH = Si-O-M (M = Si or Al) might be occurred during the extraction-stratification process.

3.3. FTIR semi-quantitative analysis

Due to the complexity of the coal structure, multiple overlapping absorption peaks exist in its infrared spectrum, and the peaks are difficult to analyze directly. Therefore, reasonable infrared structure parameters can represent the actual FTIR basic organic structure data [24]. In this paper, infrared spectra of the samples were fitted by Peakfit software, and semi-quantitative analysis was performed. The results were displayed in Fig. 3 and Table 2.

According to Lambert-Bier law, the area of the absorption peak is proportional to the content of the corresponding functional group, provided that both the concentration and thickness of the coal samples are the same. However, the above requirements are difficult to meet in practical infrared spectra analysis. Zhao et al. [25,26] calculated infrared structure parameters, such as I_a , I_b and I_c , each of which is a ratio of specific absorption peak area in the same sample, which can more reasonably represent the relative contents of the corresponding functional structures. The semiquantitative calculation formular are presented in Table 3, and the differences between the two samples in the infrared structure parameters are showed in Fig. 4.

I_{a1} and I_{a2} are defined as the ratios of peak areas of carboxyl and phenolic hydroxyl groups to the total peak areas of all functional groups respectively. I_{a3} represents the relative content of carboxyl to phenolic hydroxyl groups. As shown in Fig. 4(a), both I_{a1} and I_{a3} of LR_{YL} decrease, while I_{a2} increases significantly, indicating that the relative content of carboxyl groups decreased and phenolic hydroxyl groups increased after the extraction-stratification process, presuming that the mixed solvent attacked the C=O functional group and converted it into C-O functional group, resulting in the increase of the relative content of phenolic hydroxyl groups.

I_{b1} and I_{b2} are defined as the ratios of aliphatic hydrogens and aromatic hydrogens to the total peak areas of all functional groups respectively, and I_{b3} represents the relative change of aliphatic hydrogens to aromatic hydrogens. The value of I_{b3} can reveal the distribution of hydrogen element in the sample and is an important parameter reflecting the aromaticity of the sample. As displayed in Fig. 4(b), the relative content of both aliphatic and aromatic hydrogens in LR_{YL} is reduced by 84.7% and 62.5% respectively, indicating that extraction process affected the distribution of aliphatic and aromatic hydrogens, with a stronger effect

on aliphatic hydrogens, presenting a lower aliphatic and higher aromatic hydrogens profile.

I_{c1} is defined as the ratio of the relative content of asymmetric $-\text{CH}_2$ to $-\text{CH}_3$ functional groups in the aliphatic structure, representing the length or degree of branching of aliphatic side chains and bridge bonds. I_{c2} is defined as the ratio of the aromatic C-H to the carbon skeleton of the aromatic rings, representing the abundance of hydrogen element in the aromatic structure. The higher the value, the lower the number of substituents on the aromatic ring. I_{c3} is defined as the ratio of the sum of two isolated aromatic hydrogens (1H and 2H) to the total aromatic hydrogens, representing the proportion of aromatic rings with high substitution in the overall aromatic rings. I_{c1} reflects the distribution of hydrogen element in the aliphatic structure, while I_{c2} and I_{c3} represent the degree of substitution in the aromatic rings from different perspectives. As illustrated in Fig. 4(c), I_{c1} and I_{c2} decrease by 32.15% and 44.73%, and I_{c3} does not change much (with the increasing rate of only 6.26%) for LR_{YL} compared to YL, indicating that the distribution range of hydrogen element in the aliphatic structure increased and the degree of substitution of the aromatic rings increased with the extraction-stratification treatment.

3.4 TG-DTG analysis

As illustrated in Fig. 5(a), the mass loss of YL and LR_{YL} are 48.55% and 46.94% respectively, with a slight decrease in the mass loss of LR_{YL} compared to YL. As shown in Fig. 5(b), the difference in the maximum mass loss peak temperature between the two samples is not significant, indicating that the macromolecular network structure of the coal was not damaged during the extraction-stratification process.

Before 180 °C, the mass loss was mainly due to the release of free water and part of the bound water in the sample, as well as the heat volatilization of some physically adsorbed small molecules. Between 180 °C and 300 °C, some of the weaker intermolecular forces in the sample were destroyed. In this stage, decarboxylation, the release of higher boiling organic matter, or the removal of small molecules adsorbed in the sample by capillary action might be taken place. In addition, a pronounced mass loss rate peak is observed at 210 °C for LR_{YL} , suggesting that the extraction-stratification treatment might weaken the intermolecular forces in the coal to some extent, resulting in an increase in the internal pore size of the sample, enhancing the diffusion ability of the organic matter from the sample and making it easier for the pyrolysis process of the treated coal.

As the temperature increases, the mass loss rate of both samples reached its maximum at around 450 °C, indicating that the pyrolysis reaction of the two samples is violent at this temperature, with rapid mass loss - the release of large amounts of volatile gases and tar. And the temperature region is the main stage of cracking reaction of the organic matter in the samples. Based on DTG data, pyrolysis characteristic parameters of the samples can be obtained, as shown in Table 4. In particular, the comprehensive devolatilization index $D = [(dM/dT)_{\text{max}} - (dM/dT)_{\text{mean}}] / (T_{\text{max}} - T_i - \Delta T_{1/2})$ was calculated for both samples with reference to the literature [19]. Results present that the value of D of LR_{YL} is higher than that of YL, indicating better pyrolysis reactivity of LR_{YL} .

In order to study the pyrolysis process of the two samples in more detail, DTG curves of the samples were fitted by Peakfit software [27], and the results are displayed in Fig. 6 and Table 5. As shown in Fig. 6, before 300 °C, the bound water in the coal was released, and weaker chemical bonds such as carboxyl groups were decomposed, with bond energy less than 150 kJ/mol. The temperature range of 300-420 °C was mainly attributed to the breakage of $\text{C}_{\text{al}}-\text{O}$, S-N and S-S bonds in the samples, with bond energy in the range of 150-230 kJ/mol. The rapid pyrolysis region of coal (420-550 °C) was dominated by the release of volatile organic compounds from high temperature cracking, including the breaking of bonds such as $\text{C}_{\text{al}}-\text{C}_{\text{al}}$, $\text{C}_{\text{al}}-\text{H}$, $\text{C}_{\text{al}}-\text{O}$ and $\text{C}_{\text{ar}}-\text{N}$ in the samples with bond energy in the range of 210-320 kJ/mol, and simultaneously the stabilization of a large number of heavy macromolecular fragments by free radical reactions might be occurred, released as tar. The rapid condensation stage of coal was mainly attributed to the breaking of $\text{C}_{\text{ar}}-\text{C}_{\text{al}}$, $\text{C}_{\text{ar}}-\text{O}$, S-N and S-S bonds in the sample, in addition to the decomposition of carbonates in coal to CO_2 with bond energy in the range of 300-430 kJ/mol. When the rate of tar cracking exceeds the rate of

tar formation, the alkyl aromatic form of tar was prone to cracking and small aromatic molecules containing C-C groups were produced. After 715 °C, the temperature region was defined as the slow condensation stage, where the aromatic rings condensed to produce H₂, and a small amount of CO was also produced, derived from the reaction of coke and CO₂.

3.5 TG-FTIR

TG-FTIR diagrams of the pyrolysis products from the two samples with the heating rate of 20 °C/min are presented in Fig. 7 and Fig. 8. As shown in Fig. 7(a) and Fig. 8(a), both samples show many absorption peaks in the 500-4000 cm⁻¹ range for the pyrolysis products, suggesting that the products may exhibit several group compositions in the experimental temperature range. Overall, compared to YL, the absorption peaks intensity of the pyrolysis products is significantly higher after the extraction-stratification treatment, which might be explained by the looser pore structure of LR_{YL}, facilitating the escape of the large amount of volatile organic compounds produced during the pyrolysis process.

As illustrated in Fig. 7(b) and Fig. 8(b), the samples display weak peaks in the range of 3500-4000 cm⁻¹ at 450 °C, where the stretching vibration peak of -OH reflects the release of hydroxyl-containing compounds such as H₂O and alcohols during the pyrolysis process, where H₂O originates mainly from free water, bound water, crystalline water and water product formed in the condensation reactions during pyrolysis. Absorption peaks observed at 2800-3000 cm⁻¹ are attributed to the stretching vibrations of -CH₃ and -CH₂, demonstrating the release of aliphatic small organic compounds such as CH₄ and C₂H₆. The release of CH₄ during coal pyrolysis might be originated from the cleavage of methoxy, and the pathway of CH₄ production was likely to be the pyrolysis of methoxy in coal at higher temperature to produce free radicals (*CH₂ or *CH₃), which could be hydrogenated to produce CH₄(*CH₂/*CH₃+*H-CH₄).

The maximum absorption intensity for both samples is a vibrational peak at 2200-2400 cm⁻¹, which is associated with the release of CO₂, mainly caused by the cleavage of carboxyl functional group in the samples and/or by the scission and detachment of C-O bond. A weak absorption peak between 2000-2200 cm⁻¹ is related to the release of CO, probably derived from the cleavage of carbonyl group. A distinct absorption peak appeared in the range 1600-1900 cm⁻¹, corresponding to the C=O absorption peaks of aldehydes, ketones and organic acids. C-C skeleton vibration at 1450-1600 cm⁻¹ is attributed to the aromatic ring. Bending vibration at 1300-1400 cm⁻¹ and stretching vibration at 1000-1200 cm⁻¹ might probably be caused by aromatic ring structures containing hydroxyl groups, thus the identification of functional groups with both aromatic rings and hydroxyl can be performed. Specifically, the absorption peaks could be presumed to be caused by phenolic compounds. In addition, the absorption peak at 966 cm⁻¹ was thought to be caused by NH₃ [28].

As demonstrated in Fig. 7(c) and Fig. 8(c), at pyrolysis temperature less than 200 °C, there are clear absorption peaks for CH₄, phenols and C=O, which might be derived from the release of CH₄ adsorbed in the pore structure of the samples and the formation of small amounts of phenolic compounds, as well as the decomposition of carboxylic acids. With the increase of pyrolysis temperature, at 400-600 °C, almost all functional groups in coal pyrolysis products appeared absorption peaks, and the release of C-O, C=O, -OH, acids, phenols and alcohols mainly occurred at this stage, indicating that this interval is the main stage of pyrolysis. Among them, the absorption peaks of CO₂ and CH₄ showed the maximum intensity, indicating that the main gases released at this stage were CO₂ and CH₄. The main absorption peaks between 600-800 °C were attributed to CO₂ and CO, which were most likely due to the secondary conversion of C=O and C-O containing organics in the pyrolysis products, including chain breakage and reforming. Furthermore, the CO absorption peak was also presumed to be due to the reaction of coke with CO₂(C+CO₂-2CO) at higher temperature. In summary, the main gaseous products are H₂O, CH₄, CO₂ and CO, as well as small amounts of NH₃ during the pyrolysis process of the two samples.

3.6 Pyrolysis products distribution

Pyrolysis products from YL and LR_{YL} at 450°C were analyzed by TG-FTIR-GC/MS. Results showed that 55 organic compounds could be detected in the pyrolysis products from YL and 53 from LR_{YL}. All the compounds can be classified by their group composition into alkanes, alkenes, arenes, oxygen-containing compounds and other heteroatoms-containing compounds. And the oxygen-containing organic compounds can be subdivided into alcohols, phenols, ketones, ethers and carboxylic acids.

Fig. 9 presents the distribution of the relative content of each group composition from the two coal samples by the technology of pyrolysis. Hydrocarbons detected by GC/MS in the pyrolysis products of YL and LR_{YL} at 450 °C were mainly alkanes, alkenes and arenes, with higher relative contents of alkanes of 31.1% and 36.2%, followed by arenes of 27.1% and 22.6%, respectively. The oxygen-containing compounds were mainly alcohols and phenols, with a small difference in the relative content of alcohols and a large difference in the content of phenols (17.6% and 22.1%, respectively), speculating that the extraction-stratification treatment could expose more oxygen-containing groups and bridge bonds, facilitating their conversion to phenolic hydroxyl groups during pyrolysis process, resulting in more phenolic compounds. The reduction in the relative content of other heteroatom-containing compounds in the pyrolysis products of LR_{YL} suggested that extraction-stratification treatment could remove heteroatomic components from coal to some extent.

Fig. 10 illustrates the possible mechanisms of bond breakage in coal pyrolysis. The core of the basic structural unit of coal consists mainly of aromatic rings and a small number of hydrogenated aromatic, alicyclic and heterocyclic rings, with alkyl side chains and other small functional groups located at the periphery of the basic structure, and each group is connected to the rings by bridging bonds to form the three-dimensional macromolecular network structure of the coal. The breakage of chemical bonds and the decomposition of functional groups in coal can produce coke, tar and gaseous products [29,30]. The formation of H₂O was associated with the carboxyl and hydroxyl groups. The radical of *H could be broken off from a carboxyl group and react with *OH in another carboxyl group to produce water. At higher temperature, *H can also react with *OH in phenols or alcohols to produce water. The formation of CO₂ was also related to the decomposition of carboxyl group. In addition, a portion of CO₂ was generated by the breakage of oxygen-containing groups connected to the aromatic ring, while CO₂ can form CO and H₂O if it reacts with *H. The formation of CO was mainly derived from the decomposition of carbonyl groups and might also be associated with the disproportionation of coke with CO₂ at higher temperature (C+CO₂=2CO).

Moreover, *CH₃ could be formed by the breakage of -O-CH₃ during pyrolysis, which could react with *H to form CH₄. At higher temperature, *CH₃ could also be formed by the breakage of aliphatic C-C, and the *CH₃ could then react with *H to form CH₄. Of course, small radical fragments could combine with *H to form other stable gaseous hydrocarbons, such as C₂H₆ and C₃H₈. On the other hand, the fragments of larger molecular weight radicals generated by cleavage could combine with *H to form tar. During this process, the radicals generated by the breakage of aryl ether and oxygen-containing bridge bonds might react with *H or *OH to form phenolic or alcoholic compounds. Admittedly, oxygen-containing groups and aliphatic side chains in the macromolecular radicals can also be broken to form aliphatic and aromatic compounds. Undeniably, aromatic and aliphatic groups can also be reacted by rearrangement and condensation to produce tar and semi-coke with larger molecular weight, while releasing *H to form H₂. As pyrolysis temperature rises, the condensation reaction would be intensified, and coke could be formed.

4. Conclusion

Composition and structure characteristics and pyrolysis products distribution of Yinggema lignite (YL) and its light residue (LR_{YL}) were analyzed by Thermogravimetry-Fourier transform infrared spectrometer-Gas chromatography/mass spectrometer (TG-FTIR-GC/MS). Extraction-stratification treatment could cause the small molecules in the coal to be dissolved and some intermolecular forces to be destroyed, leading to the increase of pyrolysis reactivity, while the macromolecular network structure of the coal was not disrupted during the treatment. Main gaseous products from the pyrolysis of both samples were H₂O, CH₄, CO₂ and CO, and small amounts of NH₃. For the pyrolysis products at 450 °C, the detectable hydrocarbons by GC/MS

were mainly alkanes, olefins and aromatics, and the detectable oxygenated compounds were mainly alcohols and phenols. The extraction-stratification treatment could promote the formation of gaseous products during the pyrolysis process, with higher promotion effect on CH_4 and CO_2 , and more oxygenated bridge bonds might be exposed, leading to the formation of more phenolic compounds.

Acknowledgments

The project was supported by the special project for regional collaborative innovation from Xinjiang Uyghur Autonomous Region (2022E01057), the Scientific Research Program from Xinjiang Energy Co., LTD “Composition/structure characteristics and catalytic cracking of organic matter in middle-low rank coal in Xinjiang” and “Composition and structure analysis of low-middle rank coal in Xinjiang and its thermochemical transformation”.

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