Hydrocarbon Generation and Chemical Structure Evolution from Confined Pyrolysis of Bituminous Coal

Wu Li,* Yan-Ming Zhu, Chang-Qing Hu, Sheng-Bo Han, and Jin-Shui Wu

ABSTRACT: The molecular composition of organic matter formed during pyrolysis is complex. Fourier transform infrared spectroscopy (FTIR) is a good technique to investigate the coal chemical structural evolution. However, reports on the effects of chemical structure on the n-alkane yields and their relative functional groups are scarce in the literature. In our case, the chemical structural evolution process of bituminous coal obtained by pyrolysis at two different heating rates has been analyzed by pyrolysis-gas chromatography (Py-GC) and FTIR. Furthermore, some of the small molecular compounds (e.g., n-alkanes 24 can generate n-alkanes 20 or low-weight compounds) generated by gold-tube pyrolysis were identified using other GC techniques. Biomarkers were analyzed and compared to generated n-alkanes from the gold-tube pyrolysis experiments. We present the results of the relationship between the FTIR parameters and the molecular compositions that were analyzed. A good linear relationship can be seen between the FTIR parameters (C=O, C≡C, and C-factor values), the carbon preference index (CPI), and the ratio of the pristane content and n-C17 alkane content (Pr/n-C17). Furthermore, the n-alkane fraction of the pyrolysates, in particular pristane, phytane, n-C17 alkane, and n-C18 alkane, changed upon maturation. Our conclusions indicate that FTIR is applicable as a structural and chemical change probe to explore the pyrolysis process.

1. INTRODUCTION

Coal gold-tube pyrolysis can be used to simulate the process of coking and gasification. The coal pyrolysis compositions are normally highly complex and affected by many factors, including maceral composition, temperature, heating procedures, confining pressures, mineral matrices, and water. The products can be divided into three groups of carbon chains: C1−C4 (gas), C6−C14 (oil), and C15+. Many studies have focused on the gaseous products and the reaction kinetics. For example, the reactions and formation process of some different gases, oils, and solids generated from coal in different coal ranks have been researched using pyrolysis and advance technology.1−14 The chemical structure of the coal molecules is commonly altered under pyrolysis. Certainly, it is important to investigate the relationship between the products and their chemical structure. The reaction mechanisms for coal or kerogen and the first reactions of functional groups can be determined using laboratory experimental techniques. Furthermore, additional information on the structural evolution can be obtained through changes in the structural parameters and biomarkers during pyrolysis.

Much attention was paid to works on the same subject (chemical structure of the coal molecules) but performed with other methods. For example, studies focusing on coal geology and organic chemistry using solid-state carbon-13 nuclear magnetic resonance (13C NMR), Fourier transform infrared spectroscopy (FTIR), and XRD. These methods can provide the key information on functional groups and their structural parameters in kerogen or coal macerals.15−16 13C NMR is a useful technique to obtain the coal structure and carbon type.7−9 FTIR is an accepted technique used in materials, organic matter, and other geological studies.10−12 Some key information on the chemical structure of rocks and macerals in coal can be obtained using Micro-FTIR spectra and their indexes, particularly structural parameters of different macerals in carbon-based materials and bituminous coals.12 Some-time, FTIR has provided the molecular level information on organic matter, kerogen, and its coal tar.15−17 For example, the chemical structure of lignite coal chars during pyrolysis18 and a finding that the kerogen molecules can change into small molecular compounds based on the broken weak bonds.19 Chen et al. reviewed the applications for geoscience of Micro FTIR and reported insightful chemical information on fossils using the FTIR data.20 It was reported that there are different
conformations of chemical functional groups in macerals, such as aromatic C=O stretching, aliphatic C=O groups, C–H stretching out of plane, and C–H x stretching that can be characterized using FTIR. The aromatic content is less than the aliphatic chain content in vitrinite at the same coal rank. The analysis of kerogen and coal organic matter in different ranks has been carried out to reveal their chemical structural information. For obtaining the CH2/CH3 parameters, FTIR has also been used to research the fossil palynomorphs’ molecular chemical structure, hard coal, and deformed soft coal. Semiquantitative FTIR analysis can be used for describing the peak area ratio intensities and calculating the spectral parameters including the A-factor ratio, C-factor ratio, CH2/CH3 ratio, C=O/C=O ratio, Al/Ox ratio, Al/C=O ratio, C=C index, C=O index, fP, Ha/Hu ratio, and (R/C)u ratio. The coal molecular structures in middle–high rank coals were characterized using the FTIR data, which indicates that the aliphatic chain length of the aromatic rings shortens along with the coalification process. It has also been shown that the lower-rank coals should have a more oxygen chemical structure and longer aliphatic chains. Along with the increasing rank, the oxygen functional group contents decrease rapidly. FTIR was used to characterize the oxidative influence of NaClO on the coal molecular structure and it was postulated that the longer aliphatic chains in residues were caused by the breakage of the aromatic rings. Sun et al. compared some reactions and structures of vitrinite and inertinite, coal maceral structures obtained in pyrolysis, and found that the two macerals had different structures and products. Thus, the application of FTIR as a chemical and structural change probe in pyrolysis has been previously established. However, additional studies on the molecular composition of the organic matter during pyrolysis, especially n-alkanes, are needed, as they are not well documented in the literature. A previous study focussed on the gaseous products and kinetic parameters during pyrolysis. Few studies investigated the relationship between the FTIR parameters (C=O, C=C, and C-factor values), the carbon preference index (CPI), and Pr/n-C17. During pyrolysis, the distribution of biomarkers and aromatic compounds changes. The products generated from organic matter include gas (C1−5), liquid (C6−14), and solid (C15+). The n-alkane yields are affected by temperature, coal rank, coal chemical structure, and coal composition. Different functional groups have different n-alkane yields. The n-alkane product content increases with temperature and the value of maturity parameters becomes low. Pyrolysis-gas chromatography mass spectrometry (Py-GC/MS) is an appropriate method, which can be used to describe the major compounds and the general characteristics of organic matter in different solids. It can also be used to investigate the pyrolysis process of bituminous coal treated with high sulfur using the ionic liquid pretreatment. A broad variety of extant biomaterials and different fossils has been analyzed using laser and curie point pyrolysis-GC/MS. These techniques show the temperature effects on organic microfossils during pyrolysis. A Cambrian marine solid bitumen, which was collected from the Guangyuan area, north-western Sichuan Basin, China, has been analyzed by GC–MS and flash pyrolysis. Additionally, the coal molecular products can provide some details on the depositional environment. The molecular analysis, paleoenvironmental interpretations from the biomarker geochemistry of n-alkanes from coals in Australia and Europe, and the distributions of n-alkanes were investigated by Py-GC/MS. Using the pyrolysis experiments, the gas yields, liquid products, and solid residues of humic coals in different stages of coalification have been obtained by Nikola Vuković. The components of the liquid products were composed of n-alkyl and n-alkane aromatic structures. There are some biomarker...
parameters, pristane/n-C\textsubscript{17}, CPI (carbon preference index), pristane/phytane (Pr/Ph), and phytane/n-C\textsubscript{18}, which can be used to understand the effects of igneous dike intrusions and the perylene on sedimentary rocks. Alkanes and biomarkers were thoroughly analyzed in other refs 43 and 44, which gave insights into changes in molecules. The biomarker compositions and n-alkane changes along with maturation and the loss process for aliphatic groups through thermal cracking should be further investigated. Although the evolution of the chemical structure has been analyzed separately, there are few studies on how chemical structure affects n-alkane yields or which functional groups are altered into biomarkers (e.g., the implications of bitumen chemistry for hydrocarbon mobility were discussed). Discussion about the effects of chemical structures on n-alkane yields and their relative functional groups is scarce.

In our case, the chemical structural evolution of bituminous coal during gold-tube flash pyrolysis at two different heating rates has been obtained by Py-GC and FTIR. FTIR parameters of the coal residues, Al/OX, Al/C=C, C-factor ratio, A-factor ratio, CH\textsubscript{2}/CH\textsubscript{3} ratio, and A\textsubscript{ad}/A\textsubscript{ag} ratio, have been obtained by peak fitting and using the area ratio. Then, some small molecular compounds were identified using the GC solutions. The biomarkers were analyzed and compared with the n-alkanes generated from the gold-tube pyrolysis experiments, and the relationships between FTIR parameters and molecular compositions were analyzed. To explore the pyrolysis process, FTIR was used as the chemical and structural change probe. Furthermore, the n-alkane fraction of the pyrolysates, in particular the pristane, phytane, n-C\textsubscript{17}, and n-C\textsubscript{18} changes after maturation. It is useful to understand how the molecular chemical structure affects biomarker parameters and calculate the n-alkane content. The data and details of our case could provide information on the coal-gasification processes.

2. COAL SAMPLES AND METHODS

2.1. Coal Samples. The coal sample analyzed, namely N32, has been collected from a simple mine working-face of the Qinan Coal Mine in the Huabei Coalfield of East China in the Xiashihezi Formation. It is located in the no. 6 coalbed (Figure 1). The sample, collected from the no. 6125 coal face, was air-dried and taken in a sample-collection bag. The sample was dried at 30 °C for one day. The results of proximate and ultimate analyses of the coal sample were obtained based on the Chinese National Standards (no. GT/T 212-2008 and no. GT/T 476-2001). Measurements of vitrinite reflectance were made on polished thin sections using an Axio Imager Mlm, ZEISS. All measurements were of maximum reflectance, in oil. 50 vitrinite particles were measured. S\textsubscript{1}, S\textsubscript{2}, and T\textsubscript{max} were measured using Rock-Eval 6 equipment (France). Details of the results obtained for the coal sample (Rock-Eval parameter data, elemental analysis, and vitrinite reflectance (R\textsubscript{o,max})) are shown in Table 1.

To explore the pyrolysis process, FTIR was used as the chemical and structural change probe. Furthermore, the n-alkane fraction of the pyrolysates, in particular the pristane, phytane, n-C\textsubscript{17}, and n-C\textsubscript{18} changes after maturation. It is useful to understand how the molecular chemical structure affects biomarker parameters and calculate the n-alkane content. The data and details of our case could provide information on the coal-gasification processes.

2. COAL SAMPLES AND METHODS

2.1. Coal Samples. The coal sample analyzed, namely N32, has been collected from a simple mine working-face of the Qinan Coal Mine in the Huabei Coalfield of East China in the Xiashihezi Formation. It is located in the no. 6 coalbed (Figure 1). The sample, collected from the no. 6125 coal face, was air-dried and taken in a sample-collection bag. The sample was dried at 30 °C for one day. The results of proximate and ultimate analyses of the coal sample were obtained based on the Chinese National Standards (no. GT/T 212-2008 and no. GT/T 476-2001). Measurements of vitrinite reflectance were made on polished thin sections using an Axio Imager Mlm, ZEISS. All measurements were of maximum reflectance, in oil. 50 vitrinite particles were measured. S\textsubscript{1}, S\textsubscript{2}, and T\textsubscript{max} were measured using Rock-Eval 6 equipment (France). Details of the results obtained for the coal sample (Rock-Eval parameter data, elemental analysis, and vitrinite reflectance (R\textsubscript{o,max})) are shown in Table 1.

2.2. Gold-Tube-Con fined Pyrolysis Experiments. The pyrolysis experiments for the Qinan coal (N32) were conducted in a gold tube (Hydrocarbon Generation Kinetics Simulation Equipment). For these experiments, a total of 13 vessels with the same pressure were used. The pressure errors were controlled to less than 0.1 MPa. Our pyrolysis experiments were carried out at 2 and 20 °C/h heating rates. 26 flexible gold capsules were used for loading coal (about 100 mg). More experimental details can be found in ref 4647. The temperature was increased from 323.3 to 600.2 °C with an
approximate 20 °C interval during the 2 °C/h heating rate, and from 324.8 to 590.0 °C during the 20 °C/h heating rate. The vitrinite reflectance value of 26 coal residue samples was calculated according to ref. 47. After pyrolysis, the volatile components in the gold tube were analyzed using the method reported by Pan et al.46

2.3. FTIR Analysis. For the gold-tube pyrolysis experiments, 26 coal residue samples were collected and analyzed using a Bruker VERTEX-70. All fractions were prepared as KBr pellets. The wavenumber range of each spectrum is from 400 to 4000 cm$^{-1}$ by 4 cm$^{-1}$. Measurements were carried out twice on each sample to obtain the correct results. Assignments of different peaks for functional groups were carried out as reported in some key refs.48–50

The FTIR structural parameters (the A-factor ratio, C-factor ratio, and $A_{ar}/A_{al}$ ratio) were all calculated based on the peak areas following the standard procedures.44,46,47,51 The results of the FTIR experiments, in part (e.g.,: the Al/C ratio increasing with the $R_o$ value, decreasing $A_{ar}/A_{al}$) are investigated using statistical analysis, and then discussed accordingly, based on the literature.52

We have calculated the CH$_2$/CH$_3$ ratio using the peaks at 2920 and 2950 cm$^{-1}$ from the peak area of the 3000–2800 cm$^{-1}$ spectral region. The 1800–1000 cm$^{-1}$ spectral region, representing C=O and C=C bending modes, was, respectively, curve fitted to derive area 1800–1650, area 1650–1520, area $\sim$1714, area $\sim$1600, and area 1600–1800 cm$^{-1}$ for calculating the Al/C=C, Al/OX ratio, A-factor ratio, C-factor ratio, and $A_{ar}/A_{al}$ ratio. The examples of the curve-fitted spectra obtained using Origin 7.0 software PFM for both the aliphatic wavenumber in the 2800–3000 cm$^{-1}$ range and the C=O/C=C ratio in the 1200–1800 cm$^{-1}$ range of the coal sample at 349.7 °C are shown in Figure 2, these ranges were used for calculation of the structural ratios. All the fitted peaks are of the Gaussian type.

\[
\text{CH}_2/\text{CH}_3 = \text{area 2920 cm}^{-1}/\text{area 2950 cm}^{-1}
\]

\[
\text{Al/OX} = (\text{area 3000–2800 cm}^{-1})/(\text{area 1800–1600 cm}^{-1})
\]

\[
\text{Al/CaC} = (\text{area 3000–2800 cm}^{-1})/(\text{area 1600–1500 cm}^{-1})
\]

\[
\text{CaO/CaC} = (\text{area 1700–1600 cm}^{-1})/(\text{area 1600–1500 cm}^{-1})
\]

\[
\text{CaO cont} = (\text{area } \sim 1714 \text{ cm}^{-1})/(\text{area 1800–1600 cm}^{-1})
\]

\[
\text{CaC cont} = (\text{area } \sim 1600 \text{ cm}^{-1})/(\text{area 1800–1600 cm}^{-1})
\]

\[
A\text{-factor} = (\text{area 3000–2800 cm}^{-1})/(\text{area 3000–2800 cm}^{-1} + 1650–1520 \text{ cm}^{-1})
\]

\[
C\text{-factor} = (\text{area 1800–1650 cm}^{-1})/(\text{area 1800–1650 cm}^{-1} + 1650–1520 \text{ cm}^{-1})
\]

\[
A_{ar}/A_{al} = (\text{area 1490–1620 cm}^{-1})/(\text{area 2815–3000 cm}^{-1})
\]

3. RESULTS

3.1. FTIR Spectra of the Coal Samples. The FTIR spectra of all the coal samples and coal chars subjected to different temperature treatments during the 20 °C/h experiments exhibited peaks with good shape (Figure 3), these results facilitate easy peak fitting and qualitative calculations. Some peaks in our FTIR spectra correspond with previous studies that showed broad absorption at 3300 cm$^{-1}$. It has been assigned to the O–H stretch intermolecular bond. A weak peak at 3010 cm$^{-1}$ was attributed to aromatic C–H. The strong absorption peaks at 2950 cm$^{-1}$ and 2920 cm$^{-1}$ should be assigned to aliphatic CH$_3$, aliphatic CH$_2$, and CH$_1$. A weak absorption peak at 1710 cm$^{-1}$ was assigned to the vibrations of the C=O functional groups. The peak at about 1600 cm$^{-1}$ could be ascribed to the stretching of the chemical aromatic ring. A peak corresponding to the C–H bond of CH$_3$ and CH$_2$ deformation bending at about 1450 cm$^{-1}$ was detected and it is possibly the result of aromatic ring modes of coal organic matter. There were peaks for the CH$_3$ groups at 1375 cm$^{-1}$. The band between 1100 and 1000 cm$^{-1}$ could be assigned to aliphatic alcohols and ethers. Those peaks around 1100 cm$^{-1}$ correspond to the oxygen functional groups of aliphatic alcohol C–O and ether C=O–C stretching. The band between 900 and 700 cm$^{-1}$ was assigned to the aromatic C–H band stretching of out-of-plane bending modes. The band and peak intensities slightly decreased along with the pyrolysis temperature. There was an obvious decrease in the band at 1600 cm$^{-1}$. Figure 4 shows the peak-fitting results and the FTIR spectrum between 3000 and 2800 cm$^{-1}$, and using the area of Gaussian peaks, some structural parameters were calculated.

The ratio of area CH$_2$/area CH$_1$ provided some information on the degree of branching of the length of the aliphatic side chain. If the CH$_2$/CH$_1$ ratio is low, it means that there are more branched aliphatic chains.53 Calculations of the Al/Ox ratio, C=O/C=C ratio, C=O cont parameter, and $A_{ar}/A_{al}$ ratio can be found in a previous study.54 The A-factor ratio has been used to explain the ratio of aliphatic and aromatic peaks.55 The C-factor ratio represents the content of the carboxyl and aromatic peaks.56
The Al/OX and Al/C=C ratios obtained from the peak fitting and peak areas increased rapidly along with the vitrinite reflectance value during the 20 °C/h pyrolysis and reached a maximum at a vitrinite reflectance of 0.73% but then rapidly decreased to a low value at 1.19% R_o,max (Figure 5). After this stage, the Al/OX and Al/C=C ratios increase in the 1.19−1.81% R_o,max range; from 1.81 to 3.72% R_o there is a strong linear relationship between Al/OX and Al/C=C. The Al/C=C value was greater than the Al/OX value at the same vitrinite reflectance for all the coal samples (20 °C/h). The ratio of Area C=O/Area C=C and the C=O content values increased with the vitrinite reflectance and is the highest corresponding to 0.73% R_o,max, similar to the Al/OX and Al/C=C ratios from 0.52 to 0.73%. Both of these ratios decrease slowly from 0.73 to 3.72%. This indicates that the C=O functional group first increased and then decreased. The reason for the increase is potentially the effect of other functional groups transforming into C=O. The C=O/C=C value was observably higher than the C=O cont value near the 0.73% vitrinite reflectance, while it remained similar in other points. The C=C cont value decreases slightly between 0.52 and 0.73% R_o,max, then increases suddenly from R_o,max 0.73 to

Figure 4. Peak-fitting curves between 3000 and 2800 cm\(^{-1}\).
0.96% after which it increases slowly from 0.96 to 1.19%. Finally, the value was steady at 0.94%.

The A- and C-factors can be used to estimate the aromatization degree. When the heating rate was 20 °C/h, the A-factor increased rapidly along with vitrinite reflectance value during pyrolysis reaching a value of 0.73% of vitrinite reflectance, then decreased rapidly in the range between 0.73 and 1.19%. The A-factor increases between R_o,max 1.19 and 1.47% and then decreases at 1.81%. Figure 6 shows that after

1.81%, there was a linear relationship between the A-factor and the vitrinite reflectance. This result is consistent with the Al/C=C and Al/OX ratios. Another parameter, C-factor could be used to explain two stages with the vitrinite reflectance. It increases from R_o,max 0.524 to 0.73%, and then decreases slowly from 0.73 to 3.72%. However, the ratios were only slightly greater than the other points.

A higher structural CH_2/CH_3 ratio indicates longer aliphatic chains or more aliphatic side chains. With the 20 °C/h heating rate, the CH_2/CH_3 ratio increases along with increasing vitrinite reflectance (0.52–0.96%) and reaches a maximum value of 6. Then, it decreases suddenly between 0.96 and 1.19% and increases again but at a lower rate, indicating that there are some reactions occurring between 0.96 and 1.19% (Figure 7). There are two different values at the 0.96% point. After this point, the CH_2/CH_3 ratio is approximately 3. A previous study suggested that when the aliphatic CH_3 chains

become shorter or longer branched, the Area CH_2/Area CH_3 ratio increases, and this was confirmed in this study. Two CH_2/CH_3 stages indicate that some of the aromatic carbon has transformed into aliphatic chains and there are more aliphatic chains after the 1% point. The A_\text{ar}/A_\text{al} ratio, ranging from 1.6 to 4.0, changes with the coal rank. It shows a linear decrease from 0.52 to 0.73% and a linear increase from 0.73 to 1.19. After the 1.19% point, the ratio decreases. There was a good linear relationship between the vitrinite reflectance from 1.81 to 3.0% and the A_\text{ar}/A_\text{al} ratio. The loss of aliphatic chains, aromacity, and polycrystallization made the parameters A_\text{ar}/A_\text{al} and CH_2/CH_3 ratios change. Furthermore, the C-factor, which was used to estimate aromaticity and aliphatic content, has a minimum value at R_o 1.0%.

Figure 8 shows that the Al/OX and Al/C=C ratios at a slow heating rate (2 °C/h) first decrease at R_o 0.67–0.79%, then the Al/OX rapidly increases along with vitrinite reflectance (0.79–1.69%), while the Al/C=C also increases between 0.79 and 2.09%. After this stage, the Al/OX and Al/C=C ratios rapidly decrease and reach the lowest value at 2.52% with a final increasing trend. The relationship of Al/OX and Al/C=C ratios with vitrinite reflectance is linear (from 2.52 to 3.86%), and is consistent with the changes of the two ratios from 1.81 to 3.72% (20 °C/h). The C=C value and the C-O/C=C ratio first increase in relation to increasing vitrinite reflectance and then slowly decrease. The highest
values for both ratios are located at a vitrinite reflectance of 0.79%. The same result is found with the 20 °C/h heating cycle. The C=C cont value decreased with the increase of vitrinite reflectance from 0.67 to 0.79%, then increases suddenly when the vitrinite reflectance is between 0.79 and 1.08%. The C=C cont values reach a maximum at $R_{o,max}$ 1.69%.

When the heating rate is 2 °C/h, there were two stages for the coal samples divided by a vitrinite reflectance of 2.52%. The 7A-factor first decreases from $R_{o,max}$ 0.67 to 0.79% and increases rapidly from $R_{o,max}$ 0.79 to 2.09% during the first stage (Figure 9) but then decreases suddenly from $R_{o,max}$ 2.09 to 2.52%. During the second stage (2.52–4.45%), the A-factor increases. The relationship between vitrinite reflectance and the A-factor is linear at 2.52–3.86%. Compared to the 20 °C/h heating rate value, the 2 °C/h heating rate A-factor is higher when the vitrinite reflectance is less than 2.09%. However, the 20 °C/h A-factor value is higher than the value of the 2 °C/h heating rate when the vitrinite reflectance is greater than 2.52%. This result indicates that the heating rate has affected the FTIR parameters. The C-factor increases with the vitrinite reflectance between 0.67 and 0.79% and then decreases from 0.79 to 1.08%. The minimum C-factor value occurs at 1.08%, after which, it decreases very slowly.

3.3. Molecular Composition of the Products Generated from Coal during Pyrolysis. 3.3.1. General Characteristics. From Figure 10, it can be observed that the main constituents that are generated from coal samples are almost $n$-alkanes. There are different aliphatic compounds including $n$-alkanes and $n$-alkanes up to C$_{33}$. In this study, isoprenoids, phytane (Ph) and pristane (Pr), were found. The total ion currents of the aromatic fractions are similar (Figure 11). At the fast heating rate (20 °C/h), the total content of $n$-alkanes first increases with the heating temperatures, reaching the highest value at 408 °C, and then decreases. At the 2 °C/h heating rate, the relative amounts of $n$-alkanes show a similar trend in the pyrolysis process. The maximum value is reached at 383.8 °C.

The GC curves of the coal samples are different from each other. The temperature affects the type and content of the volatile products. However, there is a similar absorption peak position. The product content reached the highest value at about 432 °C, which is also in agreement with a previous study. He et al. found that most of the aliphatic compounds were released around 430 °C with chain lengths up to C$_{31}$, with the majority being between C$_{1}$ and C$_{5}$. Aromatic hydrocarbons were also released mostly at around 430 °C.$^{57}$

Figure 11 shows the chromatograms of the coal pyrolysis products obtained at different heating rates. When the pyrolysis temperature is low, there are fewer products. The intensity of the absorption peaks increases along with the pyrolysis temperature. The contents of $n$-C$_{16}$–$n$-C$_{30}$ moieties located at retention times between 30 and 45 min are greater than those at the other retention times. There are many types of products at 432 °C at the 20 °C/h heating rate. The peak intensities of C$_{12}$–C$_{33}$ are high, indicating that the n-C$_{12}$ to n-C$_{33}$ contents are large. At a temperature of 503.9 °C, contents of most of the $n$-alkanes decrease rapidly except for n-C$_{22}$, n-C$_{19}$, and n-C$_{16}$, and the amounts of n-C$_{12}$ and pristane remain consistently high. At a temperature of 590 °C, the $n$-alkane contents are low. This indicates that the products may be transformed into gas, which included methane, CO, C$_{2}$H$_{4}$, and CO$_{2}$. The reason for the increase and decrease in the $n$-alkane content will be discussed in the next section. The pyrolysis products obtained are similar at the fast rate 20 °C/h. However, at the same pyrolysis temperature, the peak intensities of the 2 °C/h $n$-alkanes are higher. The maximum product yield at the slow rate 2 °C/h is also higher than that of the fast rate 20 °C/h. For example, the chromatogram intensity of 371.6 °C (2 °C/h) is greater than 372 °C (20 °C/h).

3.3.2. Characterization of Pyrolysis Product and n-Alkane. Trace amounts of oil are detected in the two different heating rate pyrolysis experiments (Figure 12). The C$_{14+}$ yield increases rapidly from 0.5 to 0.96%, while the C$_{6–14}$ yields generally remain low and increase from 0.5 to 1.30%. The C$_{14+}$ yield decreases significantly from 0.96 to 1.47% and then further reduces at a lesser rate from R$_{o}$ 1.47% and higher. The yield reaches a maximum value at R$_{o}$ 1.30% because of late-stage oil cracking. In addition, the C$_{14+}$ and total oil yields first increase and then decrease, which is in agreement with the coal pyrolysis product chromatograms, possibly indicating that oil, especially n-C$_{14}$–C$_{33}$ decomposes along with the temperature. Some of the compounds transformed into gaseous products. The peak areas for n-C$_{12}$–n-C$_{16}$, n-C$_{17}$–n-C$_{19}$, n-C$_{20}$–n-C$_{24}$, and n-C$_{25}$–n-C$_{33}$ as the pyrolysis parameters are shown in Figure 13. For the 20 °C/h set of experiments, the peak area shows the same change trend with the increasing temperature. The n-C$_{12}$–n-C$_{16}$, n-C$_{17}$–n-C$_{19}$, n-C$_{20}$–n-C$_{24}$, and n-C$_{25}$–n-C$_{33}$ peak areas all first increase and then decrease through oil generation
and the late-stage oil cracking. The \( nC_{12}−nC_{16}, nC_{20}−nC_{24}, \) and \( nC_{25}−nC_{33} \) peak areas reach a maximum at 432 °C, while \( nC_{17}−nC_{19} \) reach a maximum at 480 °C. When the temperature is between 324.8 and 432 °C (first stage), the products are \( nC_{12}−nC_{16} > nC_{17}−nC_{19} > nC_{20}−nC_{24} > nC_{25}−nC_{33} \) and the area differences appeared. When the temperature is between 432 and 503 °C, the products are \( nC_{17}−nC_{19} > nC_{12}−nC_{16} > nC_{20}−nC_{24} > nC_{25}−nC_{33} \). Furthermore, the area differences for the four parameters are greatest. The temperature trend in the range between 503 and 590 °C is similar to what was seen in the first stage. Additionally, the area differences disappear with the increasing temperature. The total area intensities for the \( n \)-alkanes increase slowly between 324.8 and 372 °C and then increase rapidly to reach a maximum in the temperature range of 372−432 °C, and finally decreases over 432 °C. This is possibly caused by the cracking of the coal organic molecules or lost chains. Along with increasing temperature, the \( n \)-alkane quantities produced in the

Figure 11. GC curves of the coal samples at different temperature points (Left columns-20 °C/h, Right columns- 2 °C/h).

https://dx.doi.org/10.1021/acsomega.0c02352
ACS Omega 2020, 5, 19682−19694
early stage occurred during the second pyrolysis stage also altering the compounds into smaller molecules. The reason for the maximum $nC_{17}-nC_{19}$ in the second stage is that it was produced from the second pyrolysis of $nC_{20}-nC_{24}$ and $nC_{25}-nC_{33}$ except for the coal molecule pyrolysis. The slowly decreasing $nC_{12}-nC_{16}$ trend in the second stage and an increase after 520 °C indicate that $nC_{12}-nC_{16}$ was altered into a small molecule liquid hydrocarbon.

Comparing the product characterizations at different temperature points (20 °C/h), the product percent ratios (A, B, C, and D) were converted to explain the pyrolysis process (Figure 14). The major n-alkane compounds at different temperatures are short-chain $C_{12}-C_{16}$ and $C_{17}-C_{19}$ n-alkanes (58−87%), which increase in proportion at a maximum temperature of 524 °C. The middle-chain $C_{20}-C_{24}$ n-alkanes (7−21%) decrease with temperature and reach a minimum at 590 °C. The long-chain $C_{25}-C_{33}$ n-alkanes (8−24%) decrease to a minimum 8% at 456 °C. Compared to $nC_{12}-nC_{16}$, $nC_{20}-nC_{24}$, and $nC_{25}-nC_{33}$, the percent ratio of $nC_{17}-nC_{19}$ first increases to a maximum at 456 °C and thereafter decreases. It is easy to determine whether the maximum $nC_{17}-nC_{19}$ temperature percent ratio was the same as the minimum $nC_{25}-C_{33}$.

3.3.3. n-Alkane Biomarker Parameters. The CPI parameter, ranging from 0.8 to 1.8, increases linearly along with the low maturity levels increasing the CPI. The Py/Ph ratio ranges from 0.7 to 2.0. The trend of first increasing and then decreasing of Py/Ph corresponds to the change in the coal redox properties.

We can find that there is no obvious difference in the Pr/$nC_{17}$ and Ph/$nC_{18}$ ratio when the temperature is increased from 324 to 432 °C (Figure 16) based on the plot of the Pr/$nC_{17}$ versus Ph/$nC_{18}$. This ratio and temperature have an indirect relationship; that is, as the ratios decrease the temperature increases. The kerogen type changes from type III to an intermediary type. This indicates that the n-alkane content is high during the first stage, becoming lower when temperature is higher than 456 °C. Furthermore, small molecules are increasingly formed in the n-alkane pyrolysis. The thermal process is contrary to biodegradation.

C29 steranes, which are obtained mainly from higher plants, are different from C27 and C28 because the C27 and C28 contents mainly came from the zooplankton and phytoplankton from lacustrine deposits (Figure 17). At the beginning of pyrolysis, the C28S percent was high and the C27S began to increase with temperature. This indicates that the major hydrocarbons are formed from phytoplankton.
because of the loss of side chains. A more recent study by condensation and aromaticity increases with temperature increases along with the vitrinite re
cracking process of methyl structures to aromatic rings and the loss of alkyl chains. However, in this study, the CH2/CH3 ratio increases from 0.52 to 0.96% and decreases suddenly in the range of 0.96–1.19%. We believe that coal pyrolysis is not a simple loss of aliphatic chains, rather, a complex chemical process with different stages. From R_0 0.5 to 1.5%, the relationship between the CH2/CH3 values and vitrinite reflectance is linear with a correlation coefficient of r^2 = 0.67. There are no additional data points from 1.1 to 1.4%. In contrast to Zieger et al. Jiang et al.30 suggested that there is a U-shaped curve along with increasing vitrinite reflectance and the area CH2/area CH3 ratio steadily decreases from low-rank coal to high-rank coal.21

4. DISCUSSION

4.1. Chemical Evolution during Pyrolysis. Coal molecules include aliphatic and aromatic compounds whose compositions contain C, O, H, N, and S. Here, we show the structural evolution of complex chemical processes during coal pyrolysis. In this study, the parameters that represent aromaticity, or the degree of condensation, do not decrease linearly. The C==C parameter decreased in the range of 0.52–0.73% (20 °C/h) and 0.67–0.79% (2 °C/h) and then increased. This may be attributed to the coalification process. Jiang et al.30 found that the aromatization degree of coal increases along with the vitrinite reflectance. However, f_{x} increases to a certain extent and slowly decreases after each coalification jump. Thus, we confirm that the coal aromatic rings are altered during pyrolysis, because of coalification, and they have a different character in different vitrinite reflectance ranges. According to a previous study, the degree of aromatic condensation and aromaticity increases with temperature because of the loss of side chains. A more recent study by Zieger et al.58 indicated that there was no formation of both aromatic rings and the aliphatic components causing both the aromaticity and aliphaticity to increase. In contrast, Dun et al.29 believed that an increase in the aromaticity value is mainly caused by the high quantities of graphite-like structures or polynuclear aromatic structures.

The changes in the aliphatic structures can be evidenced through changes in the Al/OX and Al/C==C ratios. It is interesting that these parameters have the same trend when the vitrinite reflectance is in the range of 1.8–3.6% (20 °C/h). D’Angelo et al.28 suggested that the Al/OX ratio denotes the content of the aliphatic C–H stretching bands in relation to the combined contribution of the oxygen-containing groups and aromatic carbon (Ox). A larger ratio indicates that the oxygen-containing groups are low. It is consistent with the results of this study. High ratios for both the C factor and Al/ C==C indicate a highly aliphatic nature and a low-aromatic carbon content. The difference between our parameter values and the early work of Wang et al.24 is that we found that the aromatic rings transform into aliphatic or there is a loss of some aromatic contents from the molecule. This could be proven by the molecular composition of the coal chars. The CH2/CH3 and A_{al}/A_{di} ratios also indicate aliphatic changes.

The CH2/CH3 ratio with respect to the methylene groups increases from low rank to high-rank bituminous coal and is thought to be the reason for the conversion of hydroaromatic methyl structures to aromatic rings and the loss of alkyl chains.29 However, in this study, the CH2/CH3 ratio increases from 0.52 to 0.96% and decreases suddenly in the range of 0.96–1.19%. We believe that coal pyrolysis is not a simple loss of aliphatic chains, rather, a complex chemical process with different stages. From R_0 0.5 to 1.5%, the relationship between the CH2/CH3 values and vitrinite reflectance is linear with a correlation coefficient of r^2 = 0.67. There are no additional data points from 1.1 to 1.4%. In contrast to Zieger et al.58 Jiang et al.30 suggested that there is a U-shaped curve along with increasing vitrinite reflectance and the area CH2/area CH3 ratio steadily decreases from low-rank coal to high-rank coal.21

4.2. n-Alkane Generation Reactions. In our study, the n-alkane products obtained from the coal pyrolysis vary depending on temperature (Figure 11). Therefore, there are two aspects to be addressed. The first involves determining the origin of n-alkanes. The second relates to why the product yields and the related factors increase and disappear.

Results reported by Qi et al.60 indicated that compounds obtained from brown coal pyrolysis are increasingly released with increasing temperature. Small molecules and gases are subsequently created from the decomposition of these compounds. Qi et al.59 reported that the cracking process of the weaker chemical bonds in the molecular coal form the primary reactions. Earlier studies of Al Sandouk-Lincke et al.37 postulated that the compounds obtained at low temperatures were products from the process of thermodesorption than from pyrolytic cracking. Then, the quantity of monoterpenes, monocyclic aromatics, aliphatics, sesquiterpenes, bicyclic aromatics, and aliphatics would increase proportionately at higher temperatures (485–650 °C), decreasing at temperatures above 764 °C. Previously published data by Li et al.51 documented a similar trend for pyrolysis products when yields of wet gases and liquid n-alkanes reached maximum values; in their study, the generation rates were equal to the removal rates in the hydrocarbon cracking. After that stage, the generation rate for n-alkanes may be less than the cracking process rate. Thus, overall, oils first increase, reach a maximum,
and then decrease (Figure 12). Pan et al.60 carried out six pyrolysis experiments and suggested that the amount of liquid hydrocarbons (C₈–C₁₈) increases substantially with temperature in the range of 240–360 °C, and then decreases along with temperature in the range of 360–400 °C. The bitumen gas chromatograms reported by Tang et al.62 display a significant trend of a gradual shift from the heavy-end (>C₂₀) to the light-end (<C₂₀) of the normal alkane distribution with increasing thermal alteration.

Figure 18 shows the changes in the FTIR parameters with the n-alkane generation parameters. They were used to infer the maturation of organic or kerogen compounds. The C-factor and C==O values decrease linearly along with increasing CPI, while they increased linearly with increasing Pr/n-C₁₇. Additionally, the C=C values increased linearly along with the CPI and decreased linearly with Pr/n-C₁₇.

5. CONCLUSIONS

To understand how the chemical structures affect the n-alkane yields and in order to identify which functional groups are altered into biomarkers, low-rank residual coal samples were collected for carrying out gold-tube pyrolysis experiments, and they were analyzed with FTIR. The results provide some insights into the changes in the coal chemical structural molecules. The parameters that represent the aromaticity or degree of condensation do not decrease linearly. The C=C value parameters decreased in the range of 0.52–0.73% (20 °C/h) and 0.67–0.79% (2 °C/h) and then increased. The main contents of the products generated from the coal samples were n-alkanes. The aliphatic products were n-alkenes and n-alkanes up to C₃₅. Ph and Pr were detected in this study. The pyrolysis products and n-alkanes generated were characterized, and the product percent ratios (A, B, C, and D) and the n-alkane biomarker parameters were obtained. Along with increasing temperature, the n-alkane quantities produced in the early stages occurred during the second pyrolysis also and they were transformed into smaller molecules. There is a good linear relationship between the FTIR parameters (C==O index, C=C index, and C-factor ratio) the CPI, and the Pr/n-C₁₇. The study of the influence of the molecular level chemical structure changes on the n-alkane generation and biomarker parameters was found to be useful. The results of our case could shed new light on the gasification mechanisms and coal-cleaning processes.
ACS Omega http://pubs.acs.org/journal/acsodf

van Heek, K. H.; Hodek, W. Structure and pyrolysis behaviour of different coals and relevant model substances. Fuel 1994, 73, 886–896.

Brown, J. K.; Hirsch, P. B. Recent Infra-Red and X-Ray Studies of Coal. Nature 1955, 175, 229–233.

Komorek, J.; Mórga, R. Evolution of optical properties of vitrinite, sporinite and semisulfinite in response to heating under inert conditions. Int. J. Coal Geol. 2007, 71, 389–404.

Conte, P.; Spaccini, R.; Piccolo, A. State of the art of CPMAS 13C-NMR spectroscopy applied to natural organic matter. Prog. Nucl. Magn. Reson. Spectrosc. 2004, 44, 215–223.

Suggate, R. P.; Dickinson, W. W. Carbon NMR of coals: the effects of coal type and rank. Int. J. Coal Geol. 2004, 57, 1–22.

Takanohashi, T.; Kawashima, H. Construction of a Model Structure for Upper Freeport Coal Using 13C NMR Chemical Shift Calculations. Energy Fuels 2002, 16, 379–387.

Guo, Y.; Bustin, R. M. FTIR spectroscopy and reflectance of modern charcoals and fungal decayed woods: implications for studies of inertinite in coals. Int. J. Coal Geol. 1998, 37, 29–53.

Chen, Y.; Caro, L. D.; Mastalerz, M.; Schimmelmann, A.; Blandon, A. Mapping the chemistry of resinite, funiginite and associated vitrinite in coal with micro-FTIR. J. Microsc. 2013, 249, 69–81.

Mastalerz, M.; Bustin, R. M. Variation in reflectance and chemistry of vitrinite and vitrinite precursors in a series of Tertiary Coals, Arctic Canada. Org. Geochem. 1994, 22, 921–933.

Russo, C.; Stanzione, F.; Tregrossi, A.; Caijolo, A. Infrared spectroscopy of some carbon-based materials relevant in combustion: Qualitative and quantitative analysis of hydrogen. Carbon 2014, 74, 127–138.

Guo, Y.; Bustin, R. M. Micro-FTIR spectroscopy of lignitic macerals in coal. Int. J. Coal Geol. 1998, 36, 259–275.

Wu, D.; Zhang, W.; Fu, B.; Hu, G. Chemical structure and gas products of different rank coals during pyrolysis. J. Therm. Anal. Calorim. 2019, 136, 2017–2031.

Liu, J.; Jiang, Y.; Yao, W.; Jiang, X.; Jiang, X. Molecular characterization of Henan anthracite coal. Energy Fuels 2019, 33, 6215–6225.

Sun, M.; Ma, M.; Lv, B.; Yao, Q.; Gao, J.; Wang, R.; Zhang, Y.; Ma, X. Pyrolysis characteristics of ethanol swelling Shendong coal and the composition distribution of its coal tar. J. Anal. Appl. Pyrolysis 2019, 138, 94–102.

Xion, H.; Wang, H.; Kang, W.; Di, C.; Qi, X.; Zhong, X.; Wang, D.; Liu, F. The reburning thermal characteristics of residual structure of lignite pyrolysis. Fuel 2020, 259, 116226.

Liu, Q.; Hou, Y.; Wu, W.; Wang, Q.; Ren, S.; Liu, Q. New insight into the chemical structures of Huadian kerogen with supercritical ethanolation: Cleavage of weak bonds to small molecular compounds. Fuel Process. Technol. 2018, 176, 138–145.

Chen, Y.; Zou, C.; Mastalerz, M.; Hu, S.; Gasaway, C.; Tao, X. Applications of Micro-Fourier Transform Infrared Spectroscopy (FTIR) in the Geological Sciences—A Review. Int. J. Mol. Sci. 2015, 16, 30233–303250.

Chen, Y.; Mastalerz, M.; Schimmelmann, A. Characterization of chemical functional groups in macerals across different coal ranks via micro-FTIR spectroscopy. Int. J. Coal Geol. 2012, 104, 22–33.

Li, W.; Zhu, Y.; Chen, S.; Zhou, Y. Research on the structural characteristics of vitrinite in different coal ranks. Fuel 2013, 107, 647–652.

Morga, R. Chemical structure of semisulfinite and fusinite of steam and coking coal from the Upper Silesian Coal Basin (Poland) and its changes during heating as inferred from micro-FTIR analysis. Int. J. Coal Geol. 2010, 84, 1–15.

Wang, S.; Tang, Y.; Schobert, H. H.; Guo, Y. n.; Su, Y. FTIR and 13C NMR Investigation of Coal Component of Late Permian Coals from Southern China. Energy Fuels 2011, 25, 5672–5677.

Xin, H.-h.; Wang, D.-m.; Qi, X.-y.; Qi, G.-s.; Dou, G.-l. Structural characteristics of coal functional groups using quantum chemistry for quantification of infrared spectra. Fuel Process. Technol. 2014, 118, 287–295.

Dutta, S.; Hartkopf-Fröder, C.; Witte, K.; Brocke, R.; Mann, U. Molecular characterization of fossil palynomorphs by transmission micro-FTIR spectroscopy: Implications for hydrocarbon source evaluation. Int. J. Coal Geol. 2013, 115, 13–23.

Liu, X.; Song, D.; He, X.; Nie, B.; Wang, L. Insight into the macromolecular structural differences between hard coal and deformed soft coal. Fuel 2019, 245, 188–197.

D’Angelo, J. A.; Escudero, L. B.; Volkmacher, W.; Zedrow, E. L. Chemometric analysis of functional groups in fossil remains of the Dicroitum flora (Cachecta, Mendoza, Argentina): Implications for kerogen formation. Int. J. Coal Geol. 2011, 87, 97–111.

Dun, W.; Guijian, L.; Ruoyu, S.; Xiang, F. Investigation of Structural Characteristics of Thermally Metamorphosed Coal by FTIR Spectroscopy and X-ray Diffraction. Energy Fuels 2013, 27, 5823–5830.

Jiang, J.; Yang, W.; Cheng, Y.; Liu, Z.; Zhang, Q.; Zhao, K. Molecular structure characterization of middle-high rank coal via XRD, Raman and FTIR spectroscopy: Implications for coalification. Fuel 2019, 239, 559–572.

Jing, Z.; Rodrigues, S.; Strounina, E.; Li, M.; Wood, B.; Underschultz, J. R.; Esterle, J. S.; Steel, K. M. Use of FTIR, XPS, NMR to characterize oxidative effects of NaClO on coal molecular structures. Int. J. Coal Geol. 2019, 201, 1–13.

Sun, Q.; Li, W.; Chen, H.; Li, B. The variation of structural characteristics of macerals during pyrolysis. Fuel 2003, 82, 669–676.

Dieckmann, V.; Horsfield, B.; Schenk, H. J. Heating rate dependency of petroleum-forming reactions: implications for compositional kinetic predictions. Org. Geochem. 2000, 31, 1333–1348.

Robinson, N.; Eglinton, G.; Lafferty, C. J.; Snape, C. E. Comparison of alkane released from a bituminous coal via hydropyrolysis and low temperature hydrogenation. Fuel 1991, 70, 249–253.

Yao, Q.; Li, Y.; Tang, X.; Gao, J.; Wang, R.; Zhang, Y.; Sun, M.; Ma, X. Separation of petroleum ether extracted residue of low temperature coal tar by chromatography column and structural feature of fractions by TG-FTIR and PY-GC/MS. Fuel 2019, 245, 122–130.

Liang, P.; Qin, X.; Bai, G.; Wu, Z.; Sun, D.; Zhang, Y.; Jiao, T. Effects of ionic liquid pretreatment on pyrolysis characteristics of a high-sulfur bituminous coal. Fuel 2019, 258, 116134.

Sandouk-Lincke, N. A.; Schwarzbauer, J.; Hartkopf-Fröder, C.; Volk, H.; Fuentes, D.; Young, M.; Littke, R. The effect of different pyrolysis temperatures on organic microfossils, vitrinite and amber—A comparative study between laser assisted- and Curie Point-pyrolysis—gas chromatography/mass spectrometry. J. Anal. Appl. Pyrolysis 2014, 107, 211–223.

Zhang, Z.; Hu, W.; Song, X.; Zhang, C.; Zhang, Q.; Jin, J. A comparison of results from two different flash pyrolysis methods on a solid bitumen sample. Org. Geochem. 2014, 69, 36–41.

Guo, Q.; Littke, R.; Ziegler, L. Petrographical and geochemical characterization of sub-bituminous coals from mines in the Cesar-Rancheria Basin, Colombia. Int. J. Coal Geol. 2018, 191, 66–79.

Izart, A.; Palhol, F.; Gleixner, G.; Elie, M.; Blaise, T.; Suarez-Ruiz, I.; Sachsenhofer, R. F.; Privalov, V. A.; Panova, E. A. Palaeoclimate reconstruction from biomarker geochemistry and stable isotopes of n-alkanes from Carboniferous and Early Permian humic coals and limnic sediments in western and eastern Europe. Org. Geochem. 2012, 43, 125–149.

Izart, A.; Suarez-Ruiz, I.; Bailey, J. Palaeoclimate reconstruction from petrography and biomarker geochemistry from Permian humic coals in Sydney Coal Basin (Australia). Int. J. Coal Geol. 2015, 138, 145–157.

Vuković, N.; Životić, D.; Mendoza Filho, J. G.; Kravič-Stevović, T.; Hámor-Vidó, M.; Mendonça, J. D. O.; Stojanović, K. The assessment of maturation changes of humic coal organic matter —
Insights from closed-system pyrolysis experiments. *Int. J. Coal Geol.* **2016**, *154−155*, 213−239.

(43) Arora, A.; Dutta, S.; Gogoi, B.; Banerjee, S. The effects of igneous dike intrusion on organic geochemistry of black shale and its implications: Late Jurassic Jhuran Formation, India. *Int. J. Coal Geol.* **2017**, *178*, 84−99.

(44) Suzuki, N.; Yessalina, S.; Kikuchi, T. Probable fungal origin of perylene in Late Cretaceous to Paleogene terrestrial sedimentary rocks of northeastern Japan as indicated from stable carbon isotopes. *Org. Geochem.* **2010**, *41*, 234−241.

(45) Malachowska, A.; Mastalerz, M.; Hampton, L.; Hupka, J.; Drobiak, A. Origin of bitumen fractions in the Jurassic-early Cretaceous Vaca Muerta Formation in Argentina: insights from organic petrography and geochemical techniques. *Int. J. Coal Geol.* **2019**, *205*, 155−165.

(46) Pan, C.; Geng, A.; Zhong, N.; Liu, J.; Yu, L. Kerogen pyrolysis in the presence and absence of water and minerals: Amounts and compositions of bitumen and liquid hydrocarbons. *Fuel* **2009**, *88*, 909−919.

(47) Sweeney, J. J.; Burnham, A. K. Evaluation of a simple model of vitrinite reflectance based on chemical kinetics (1). *AAPG Bull.* **1990**, 74, 1559−1570.

(48) Painter, P. C.; Snyder, R. W.; Pearson, D. E.; Kwong, J. Fourier transform infrared study of the variation in the oxidation of a coking coal. *Fuel* **1980**, *59*, 282−286.

(49) Painter, P. C.; Snyder, R. W.; Stassinis, M.; Coleman, M. M.; Kuehn, D. W.; Davis, A. Concerning the Application of FT-IR to the Study of Coal: A Critical Assessment of Band Assignments and the Application of Spectral Analysis Programs. *Appl. Spectrosc.* **1981**, *35*, 475−485.

(50) Wang, S.-H.; Griffiths, P. R. Resolution enhancement of diffuse reflectance i.r. spectra of coals by Fourier self-deconvolution: 1. C-H stretching and bending modes. *Fuel* **1985**, *64*, 229−236.

(51) Ibarra, J.; Muñoz, E.; Moliner, R. FTIR study of the evolution of coal structure during the coalification process. *Org. Geochem.* **1996**, *24*, 725−735.

(52) van Krevelen, D. W., *Coal*; Elsevier: New York, 1993.

(53) Lin, R.; Patrick Ritz, G. Studying individual macerals using i.r. microspectrometry, and implications on oil versus gas/condensate proneness and “low-rank” generation. *Org. Geochem.* **1993**, *20*, 695−706.

(54) Zodrow, E. L.; D’Angelo, J. A.; Mastalerz, M.; Keefe, D. Compression—cuticle relationship of seed ferns: Insights from liquid−solid states FTIR (Late Palaeozoic—Early Mesozoic, Canada−Spain−Argentina). *Int. J. Coal Geol.* **2009**, *79*, 61−73.

(55) Iglesias, M. J.; Jimenez, A.; Laggoun-Defarge, F.; Suarez-Ruiz, I. FTIR Study of Pure Vitrains and Associated Coals. *Energy Fuels* **1995**, *9*, 458−466.

(56) Song, H.; Liu, G.; Zhang, J.; Wu, J. Pyrolysis characteristics and kinetics of low rank coals by TG-FTIR method. *Fuel Process. Technol.* **2017**, *156*, 454−460.

(57) He, Q.; Wan, K.; Hoadley, A.; Yeasmin, H.; Miao, Z. TG−GC−MS study of volatile products from Shengli lignite pyrolysis. *Fuel* **2015**, *156*, 121−128.

(58) Odeh, A. O. Qualitative and quantitative ATR-FTIR analysis and its application to coal char of different ranks. *J. Fuel Chem. Technol.* **2015**, *43*, 129−137.

(59) Zieger, L.; Littke, R.; Schwarzhauser, J. Chemical and structural changes in vitrinites and megaspores from Carboniferous coals during maturation. *Int. J. Coal Geol.* **2018**, *185*, 91−102.

(60) Qi, Y.; Hann, W.; Subagyno, D. J. N.; Fei, Y.; Marshall, M.; Jackson, W. R.; Patti, A. F.; Chaffee, A. L. Characterisation of the products of low temperature pyrolysis of Victorian brown coal in a semi-continuous/flow through system. *Fuel* **2018**, *234*, 1422−1430.

(61) Li, E.; Pan, C.; Yu, S.; Jin, X.; Liu, J. Hydrocarbon generation from coal, extracted coal and bitumen rich coal in confined pyrolysis experiments. *Org. Geochem.* **2013**, *64*, 58−75.

(62) Tanj, Y.; Jenden, P. D.; Nigrini, A.; Teerman, S. C. Modeling Early Methane Generation in Coal. *Energy Fuels* **1996**, *10*, 659−671.