Application of Chemometrics for Coal Pyrolysis Products by Online py-GC×GC–MS

Hao Yin,* Jie Lu,* Guijian Liu,* Zhiyuan Niu, Xiangping Zha, Dun Wu, Airong Feng, and Yanyun Hu

ABSTRACT: Investigations on the molecular composition of coal pyrolysis products can help us to improve nonfuel utilization of coal. Meanwhile, the molecular composition of coal pyrolysis products is also influenced by the characteristics and depositional environment of coal. However, due to the extremely complex nature of coal, direct investigation of the molecular composition of coal pyrolysis products is still a challenge. In the present work, the data of the molecular composition of bituminous coal pyrolysis products are obtained by online pyrolysis coupled to comprehensive two-dimensional gas chromatography and mass spectrometry (online py-GC×GC–MS) and are divided into nine molecular groups depending on the aromaticity of the pyrolysis products and separating power of the GC×GC–MS. Chemometric tools, hierarchical cluster analysis, and principal component analysis are employed to reveal the correlations among the molecular composition of coal pyrolysis products and coal characteristics. The results show that the nine molecular groups of bituminous coal pyrolysis products can be divided into two clusters, the “aromatic group” and the “aliphatic group”, and that the eight coals are divided into three clusters, all of which can be interpreted by the depositional environments and δ13CVPDB values of coals. Moreover, a simple and empirical equation for estimation of coal tar from hydropyrolysis can be obtained depending on the chemometric results of the molecular composition of the coal pyrolysis products. By application of chemometrics, the molecular composition of coal pyrolysis products can provide preference to industrial utilization of coal.

INTRODUCTION

It is generally accepted that coal is one of the nonrenewable energy sources, which also leads to catastrophic global warming.1–3 Nonfuel utilization of coal for producing chemicals and materials is a better use of coal.4,5 A current prospect for the chemical industry suggests that it would be prudent to rethink of coal as a source of aromatic chemicals instead of petroleum because coal has a higher level of condensed aromatic composition than petroleum.6–9 Thus, a quantitative description of the molecular composition of coal pyrolysis products would be necessary for producing chemicals and controlling the particulate matter of air pollutants.10–14 In addition, the molecular composition of pyrolysis products can be helpful in describing the occurrence and characteristics of coals.

“Mass spectrometry (MS)” is a method for determining the detailed molecular composition of coal pyrolysis products.15 Furthermore, time-of-flight mass spectrometry (TOFMS) coupled with comprehensive two-dimensional gas chromatography (GC×GC) can also provide a powerful tool for separation and identification of molecular components.16–24 Koolen et al.25 analyzed some coal tar samples and observed approximately 250 peaks by GC–MS compared to 6,600 compounds by GC×GC-TOFMS and more than 14,000 mass spectral peaks by Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS), which indicates the prospect of using GC×GC-TOFMS for identification of coal molecular composition.

Due to the complexity of coal pyrolysis products, thousands of compounds could be observed by GC×GC-TOFMS. Chemometrics, including hierarchical cluster analysis (HCA) and principal component analysis (PCA),26,27 have been employed to determine the relationship between different coals and other various conditions based on the coal properties, proximate and ultimate analyses, trace elements based on ash composition, kinetics of coal pyrolysis, CO, benzene, cresols, and long-chain aliphatic compounds.28–34 Li et al. and Yu et al.35,36 identified the molecular composition of coal extraction products with FT-ICR MS and Orbitrap MS and obtained in-depth statistical results for seven classes (CH,
Table 1. Proximate and Ultimate Analyses, O/C and H/C Ratios, and Values of δ$^{13}$C$_{VPDB}$ of 11 Coal Samples$^a$

|          | ultimate analysis (wt %) | proximate analysis (wt %) | δ$^{13}$C$_{VPDB}$ (%) |
|----------|--------------------------|---------------------------|------------------------|
|          | C$_{daf}$   | H$_{daf}$   | N$_{daf}$   | O$_{daf}$   | S$_{daf}$ | O/C | H/C | M$_{daf}$ | V$_{daf}$ | A$_{daf}$ | F-C$_{daf}$ | δ$^{13}$C$_{VPDB}$ |
| XQ4      | 84.68  | 5.53  | 1.49  | 7.51  | 0.79  | 0.070 | 0.78 | 1.77  | 36.78  | 8.05  | 53.4  | −23.23 |
| XQ5      | 84.99  | 6.09  | 1.31  | 6.7   | 0.91  | 0.063 | 0.86 | 1.29  | 41.61  | 9.48  | 47.62 | −23.33 |
| XQ6      | 84.81  | 5.69  | 1.37  | 7.29  | 0.84  | 0.066 | 0.81 | 1.64  | 38.90  | 9.00  | 50.46 | −22.97 |
| XQ7_1    | 84.69  | 5.80  | 1.16  | 7.69  | 0.66  | 0.071 | 0.82 | 1.63  | 38.23  | 9.51  | 50.63 | −22.95 |
| XQ7_2    | 84.83  | 5.58  | 1.40  | 7.77  | 0.42  | 0.069 | 0.79 | 1.87  | 35.94  | 8.12  | 54.07 | −22.94 |
| XQ8      | 84.64  | 5.71  | 0.73  | 8.09  | 0.36  | 0.072 | 0.81 | 1.75  | 37.79  | 18.11 | 52.15 | −23.11 |
| XQ11_2   | 84.47  | 5.56  | 1.45  | 7.55  | 0.97  | 0.071 | 0.79 | 1.68  | 35.23  | 8.56  | 54.53 | −23.91 |
| XQ13_1   | 84.62  | 5.76  | 1.44  | 7.21  | 0.37  | 0.064 | 0.82 | 1.57  | 41.77  | 20.24 | 45.45 | −23.54 |
| BC       | 82.21  | 6.19  | 1.21  | 9.91  | 0.48  | 0.091 | 0.91 | 1.26  | 24.64  | 14.51 | 59.59 |
| AC       | 88.11  | 4.01  | 1.33  | 5.99  | 0.56  | 0.051 | 0.54 | 2.31  | 11.78  | 13.14 | 72.77 |
| NC       | 92.86  | 1.31  | 1.07  | 4.53  | 0.23  | 0.036 | 0.16 | 5.73  | 4.75   | 6.94  | 82.58 |

$^a$daf: dry ash free; ad: air dried.

**RESULTS AND DISCUSSION**

**General Characteristics of Coals.** Based on the carbon content, coals can be classified into four major types or ranks according to the U.S. Department of Energy: anthracite (carbon content 86–97%), bituminous coal (45–86%), subbituminous coal (35–45%), and lignite (25–35%). In the present work, all eight coals from the Xieqiao coal mine belong to the bituminous coal category (Table 1). BC belongs to the bituminous coal category, and AC and NC belong to the anthracite category.

The atomic ratios of O/C and H/C of the eight coals from the Xieqiao coal mine are between BC and AC (Figure 1 a). The area ratios of toluene to benzene (T/B) and xylene to benzene (X/B) for the 11 coals are illustrated in Figure 1 b, which are calculated by the area values of benzene, toluene, and xylene in Figure 2. The ratios of T/B and X/B can describe the degree of branching of coal. Although the O/C and H/C of the eight coals are so close and are between BC and AC, the differences in T/B and X/B of the eight coals are obvious as most of the eight coals are under the line connecting BC with NC, except for XQ7_2 and XQ5.

**Molecular Groups by GC×GC-TOFMS.** The GC×GC-TOFMS results are presented in bubble plots where the size of the bubble represents the area of each compound (Figure 2). In Figure 2, the X-axis is the first-dimension retention time in seconds (t$_r$1) and the Y-axis is the second-dimension retention time in seconds (t$_r$2). Coal pyrolysis products are separated by their boiling points in the first dimension and by their polarities in the second dimension. Moreover, XQ13_1 has the greatest number of chromatographic peaks ($n = 602$).

To simplify the data processing and chemometric analysis, the chromatographic peaks of assigned possible compounds of the coal pyrolysis products are grouped into 10 molecular groups of hydrocarbon classes based on their aromaticity. The 10 molecular groups are benzene, toluene, xylene, C$_3$_1RAs (one-ring aromatics with alkyl branches where the carbon number is $\geq 3$), P$_2$RAs (two-ring aromatics), P$_3$RAs (three-ring aromatics), P$_4$RAs (four-ring aromatics), other_2RAs (compounds in between 2- and 3-ring aromatics), paraffins_olefins (paraffins and olefins), and phenols_other1RAs (phenols and other one-ring aromatics other than C$_3$_1RAs). The 10...
molecular groups are illustrated in Figure 2. It should be noted that we focused on nine molecular groups in the present work excluding P_4RAs because only three coal samples (XQ11_2, XQ13_1, and BC) had the P_4Ras molecular group.

The relative ratios of the peak area for each molecular group to the total peak area for the 11 coals have been calculated and illustrated using a spider chart (Figure 3). The relative amounts of the paraffins_olefins in XQ_6, XQ7_1, XQ7_2, and BC are obviously higher than in the other coals. Meanwhile, the relative amounts of the benzene group in XQ_6, XQ7_1, XQ7_2, and BC are obviously lower than in the others. According to previous work on the past depositional environments in the research area, both the lenticular bedding and the wave bedding are evidence of a tidal depositional environment with the interdistributary bay and lake deposits.37−45

Because paraffin and olefin are transformed from epicuticular waxes of woods and mainly from lipids in algae,46 the tidal depositional environment of coal leads to a relatively higher amount of paraffin and olefin in XQ6, XQ7_1, and XQ7_2.

Figure 2. Bubble plots of 10 molecular groups of coal pyrolysis products (benzene, toluene, xylenes, C3_1RAs, P_2RAs, P_3RAs, P_4RAs, other_2RAs, paraffins_olefins, and phenols_other1RAs) for the 11 coals.

Figure 3. Spider chart of the relative ratios of the nine molecular groups for the 11 coals.
Chemometric Analysis. HCA and PCA for the nine molecular groups of pyrolysis products of each bituminous coal reveal correlations that are shown in Figure 4. Two clusters have been distinguished by HCA and component 1 (representing 60.033% of the contribution to the total data variance) of PCA. The first cluster is named the "aromatic group" and includes P_2RAs, P_3RAs, other_2RAs, and benzene, as they are all related by their aromatic structure. The second cluster is named as the "aliphatic group" and includes C3_1RAs, paraffins_olefins, phenols_other1RAs, xylenes, and toluene, as they are related by their aliphatic structure. Figure 5 shows the relative amounts of aromatic and aliphatic groups and the δ13CVPDB values of the eight coals.

Coal is deemed to be a heterogeneous mixture of plant remains transformed from Paleozoic plants by microbial and other diagenetic activities. The main aromatic compounds in coal are the degradation products from cellulose and lignin.47-48 The most common aliphatic compounds in coal are the degradation products from resinites, ambers, cuticles of leaf material, and algae.46-48 The δ13CVPDB values of marine plants are higher than in woods.46 Thus, the higher relative aliphatic compound content of coal leads to higher δ13CVPDB values in coal. Pearson’s correlation between the relative ratio of the aromatic group in the pyrolysis products and the δ13CVPDB values of the eight coals is calculated to be −0.975.

It is obviously shown that the molecular groups of other_2RAs, P_2RAs, and P_3RAs have a tight correlation (Figure 4), which is conjectured to be from a close source of cellulose and lignin of higher plant remains, in all probability.48

The coal hydropyrolysis for both XQ8 and XQ13_1 was investigated by Wang et al.49 They analyzed different coal tar (CT) samples under the same reaction conditions of temperature, time, and operating pressure (the detailed data are shown in the Supporting Information). It was also conjectured that the higher content of aromatic compounds needed higher reaction temperatures and longer reaction times, but molecular evidence of aromatic groups was not provided.

In the present work, the relative ratio of aromatic groups in XQ13_1 is higher than in XQ8 (Figure 5), so it follows that the higher relative content of aromatic groups in pyrolysis products leads to higher CT and longer reaction time under the reaction temperature of 460 °C, when similar O/C and H/C ratios in coals are produced by hydropyrolysis. Meanwhile, the δ13CVPDB value of XQ13_1 is lower than that of XQ8 (Figure 5), which also means that there is a higher relative content of aromatic groups in XQ13_1 than in XQ8 because there is negative Pearson’s correlation between the relative ratio of aromatic groups in the pyrolysis products and the δ13CVPDB values of coal.

If there is a linear relationship between the relative ratio of aromatic groups in coal pyrolysis products (x, 0 ≤ x ≤ 1) and the CT from coal hydropyrolysis (y, 0% ≤ y ≤ 100%), then, under a factor of reaction condition (A = dy/dx), the formula can be expressed as

\[ f_y = A \times f_x + b \]  

(1)

Thus, the three lines are fitted for three different reaction conditions (Figure 6).
Thus, the values of \( A \) and \( b \) for three conditions are obtained from Figure 6 and are shown in Table 2, and then, binomial fitting is performed for \( A \) and \( b \) (Figure 7).

### Table 2. Values of \( A \) and \( b \) for Three Different Conditions

| Condition | \( A \)     | \( b \)     |
|-----------|-------------|-------------|
| condition I | -18.385 | 58.737      |
| condition II | 5.9701 | 55.891      |
| condition III | 2.7137 | 60.777      |

Thus

\[
b = -0.0664A^2 - 0.9336A + 63.786
\]

Formula 2 is substituted into formula 1, and then, the empirical formula is obtained as formula 3:

\[
y = A \cdot x + (-0.0664A^2 - 0.9336A + 63.786)
\]

It is noted that the empirical formula 3 is inaccurate because it has so little experimental data for coal hydropyrolysis.

HCA and PCA also reveal the classification of eight bituminous coals, which is shown in Figure 8. The eight coals are divided into three clusters by component 2 (representing 22.324% of the contribution to the total data variance). XQ6, XQ7-1, and XQ7-2 are in the first cluster. XQ4, XQ5, and XQ8 are in the second cluster, and XQ11-2 and XQ13_1 are in the third one. According to previous work on the depositional environments,\(^{37-42}\) the coals in the first cluster belong to a tide depositional environment with the interdistributary bay and lake deposits, while the coals in the second cluster belong to a distributary channel depositional environment, and the coals in the third cluster belong to a floodplain depositional environment. In addition, according to the \( \delta^{13}C_{VPDB} \) values of the eight coals (Figure 5), the \( \delta^{13}C_{VPDB} \) values of the first-cluster coals are the highest among the three clusters and the \( \delta^{13}C_{VPDB} \) values of the third-cluster coals are the lowest.

Above all, according to the chemometric results of the eight bituminous coals and formula 3 given above, the bituminous coals formed in a floodplain depositional environment have more superiority than the coals formed in a distributary channel depositional environment in hydropyrolysis because the relative ratios of aromatic groups in the coal pyrolysis products are different.

### CONCLUSIONS

Chemometric tools, including HCA and PCA, can extract information on the molecular composition of coal pyrolysis products by the powerful separation and identification processes that can be achieved by GC×GC-TOFMS.

Eight bituminous coals from the Xieqiao coal mine have been analyzed in the same manner as other three coals, BC, AC, and NC. The nine molecular groups of coal pyrolysis products are obtained and separated by online py-GC×GC–MS. These nine molecular groups are divided into two clusters, that is, the “aromatic group” and “aliphatic group”, by the application of HCA and PCA. Meanwhile, the eight bituminous coals are divided into three clusters depending on the molecular composition of their pyrolysis products, which are interpreted and confirmed by their depositional environments and \( \delta^{13}C_{VPDB} \) values.

Moreover, when similar O/C and H/C ratios of bituminous coals are produced by hydropyrolysis, the coal tar of coal hydropyrolysis can be estimated by the relative content of aromatic groups. The chemometric results show that coal formed in a floodplain depositional environment has more superiority than coal formed in a distributary channel depositional environment when these coals are exposed to hydropyrolysis.

By application of chemometrics, the molecular composition of coal pyrolysis products will extract information about the characteristics of coal and provide preference to industrial utilization of coal.

### EXPERIMENTAL SECTION

**Material and Geological Setting.** Eight coal samples from different strata (Table 1) were collected from the Xieqiao coal mine, Huainan coal field, Anhui province, China. Three reference coals, including natural coke (NC), anthracite (AC), and bituminous coal (BC),\(^{30}\) were also collected from the Huainan coal field. Raw coal samples were air-dried and ground to a particle size of \( \leq 100 \) mesh. The proximate and ultimate analyses of these samples were carried out according to GB/T212-2008 and GB/T476-2008 (Table 1).

**Geological Setting.** To interpret the detailed depositional environment of the coal samples, a literature review of Chinese articles, including Geological Survey memoirs, on the sedimentary textures of the Xieqiao coal mine was conducted. The Huainan coal field is located in the southeastern margin of the Carboniferous-Permian coal-accumulating region of north-
ern China. The coal-bearing sequences in the present work occur in a stratigraphic order from the lower Shihezi Formation (nos. 4, 5, 6, 7, 8 coal seams) to the upper Shihezi Formation (nos. 11, 12, 13 coal seams) in the early Permian. The depositional environment of these coal seam formations changed from the lower delta plain to transitional lower delta plain-upper delta plain over time. Both the nos. 4 coal seam (XQ4) and no. 5 coal seam (XQ5) are covered by tabular cross-beded sedimentary rocks with distributary channel deposits. The no. 6 coal seam (XQ6) occurs above mudstone with lenticular bedding and interdistributary bay deposits. The no. 7_1 coal seam and no. 7_2 coal seam (XQ7_1 and XQ7_2) occur between two sedimentary rocks with wave-bedding and lake and swamp deposits. The no. 8 coal seam (XQ8) is covered by trough cross-beded sandstone with distributary channel deposits. The no. 11_2 coal seam (XQ11_2) formed above trough cross-beded sedimentary rock with floodplain deposits, which were in the branched fluvial system near the continent on the alluvial-deltaic plain but not in the middle of the floodplain. The no. 13_1 coal seam (XQ13_1) formed in the anastomosing fluvial system close to the sea on the alluvial-deltaic plain, which was overlain by tabular cross-beded sedimentary rocks in the middle of floodplains and swamps.

**Online Pyrolysis-GC×GC-TOFMS.** The online pyrolysis-GC×GC system includes a pyrolyzer with a fixed furnace (Pyrojector II, SGE, Inc.) and GC×GC-TOFMS (Leco Corp.). The pyrolysis temperature is set at 700 °C with helium as the carrier gas. The transfer tube of the pyrolyzer is placed directly into the GC inlet to transfer coal pyrolysis products to the GC column. Then, 2.0 mg of each coal sample is weighed and packed in a tin capsule and then ash-combusted in excess oxygen at 1080 °C in an elemental analyzer (Haiyu-xinhua Co. Ltd, Beijing, China). The resulting CO2 is analyzed online with ThermoFinnigan Delta plus (ThermoFinnigan, Bremen, Germany). The carbon isotope compositions of CO2 are reported in the standard δ notation on the VPDB scale. The repeatability of the total analytical procedure is in the range of 0.1−0.2‰. The experiments are conducted following the analytical method described in Zha et al. The δ13CVPDB values of coal samples are presented in Table 1.

**Carbon Isotope Analysis.** Coal samples (approx. 200–600 μg) are weighed and packed in a tin capsule and then flash-combusted in excess oxygen at 1080 °C in an elemental analyzer (Haiyu-xinhua Co. Ltd, Beijing, China). The resulting CO2 is analyzed online with ThermoFinnigan Delta plus (ThermoFinnigan, Bremen, Germany). The carbon isotope compositions of CO2 are reported in the standard δ notation on the VPDB scale. The repeatability of the total analytical procedure is in the range of 0.1−0.2‰. The experiments are conducted following the analytical method described in Zha et al.

**Statistical Analysis.** The Pearson product–moment correlation coefficient (Pearson’s correlation), γ, is widely used in statistical analysis as a measure of the degree of linear dependence on two variables (X and Y). In the present work, it is used to build the correlation relationship between the molecular composition of coal pyrolysis products and coal characteristics using HCA and PCA. The formula for γ is as follows:

\[
\gamma = \frac{\sum_{i=1}^{n} (X_i - \bar{X})(Y_i - \bar{Y})}{\sqrt{\sum_{i=1}^{n} (X_i - \bar{X})^2} \sqrt{\sum_{i=1}^{n} (Y_i - \bar{Y})^2}}
\]  

Figure 8. Dendrogram of HCA (left) and the loading plot of PCA (right) for the eight coals. (In the HCA dendrogram, the eight coals are listed along the left vertical axis and the horizontal axis shows the similarity measures among the eight coals with the default range of 0−25. In the PCA, the component scores of the eight coals for both component 1 and component 2 are in the default range of −1 to 1.)
Pearson’s correlation and a two-sample t-test of variables are calculated using IBM SPSS Statistics Version 19.

HCA is designed to identify relatively homogeneous groups of variables (coals or molecular groups) based on the molecular compositions of coal pyrolysis products, using an algorithm that starts with each variable in a separated cluster and combines clusters until only one is left. HCA is also calculated using SPSS with the parameters of Pearson’s correlation for interval data and the cluster method of between-group linkages. Similarly, measures of each variable between the clusters are generated by the proximity procedure with the default range of 0–25, when the clusters are joined.

PCA accounts for patterns of variation in coals or molecular groups based on the molecular composition of coal pyrolysis products in a single set of major components. The major components are the scale values, which are optimal with respect to the principal component solution, when these scale values are assigned to each category of every variable (coals or molecular groups). PCA is also performed using SPSS with the cluster method of between-group linkages and fixing two factors for factor extraction and 25 iterations to achieve maximum iterations for convergence. The component scores of coals or molecular groups to major components in the default range of −1 to 1 are calculated to reveal the patterns among the coals or molecular groups.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at [https://pubs.acs.org/10.1021/acsomega.0c05359](https://pubs.acs.org/10.1021/acsomega.0c05359).

Detailed hydropyrolysis conditions for XQ8 and XQ13.1 investigated by Wang et al. with the coal tar yields (PDF)

## AUTHOR INFORMATION

### Corresponding Authors

Xiangping Zha — CAS Key Laboratory of Crust-Mantle Materials and the Environments, School of Earth and Space Sciences, University of Science and Technology of China, Hefei 230026, China

Hao Yin — CAS Key Laboratory of Crust-Mantle Materials and the Environments, School of Earth and Space Sciences, University of Science and Technology of China, Hefei 230026, China; Mass Spectrometry Lab, Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Hefei 230026, China; orcid.org/0000-0002-4328-4707; Email: yinhao@ustc.edu.cn

Jie Lu — National High Magnetic Field Laboratory, Florida State University, Tallahassee, Florida 32310-4005, United States; Email: jielu@magnet.fsu.edu

Guijian Liu — CAS Key Laboratory of Crust-Mantle Materials and the Environments, School of Earth and Space Sciences, University of Science and Technology of China, Hefei 230026, China; Email: lgi@ustc.edu.cn

### Authors

Zhiyuan Niu — CAS Key Laboratory of Crust-Mantle Materials and the Environments, School of Earth and Space Sciences, University of Science and Technology of China, Hefei 230026, China

Xiangping Zha — CAS Key Laboratory of Crust-Mantle Materials and the Environments, School of Earth and Space Sciences, University of Science and Technology of China, Hefei 230026, China

Dun Wu — CAS Key Laboratory of Crust-Mantle Materials and the Environments, School of Earth and Space Sciences, University of Science and Technology of China, Hefei 230026, China

Airong Feng — Mass Spectrometry Lab, Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Hefei 230026, China

Yanyun Hu — Mass Spectrometry Lab, Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Hefei 230026, China

Complete contact information is available at: [https://pubs.acs.org/10.1021/acsomega.0c05359](https://pubs.acs.org/10.1021/acsomega.0c05359)

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