

Insight into the Compositional Features of Organic Matter in Xilinguole Lignite through Two Mass Spectrometers

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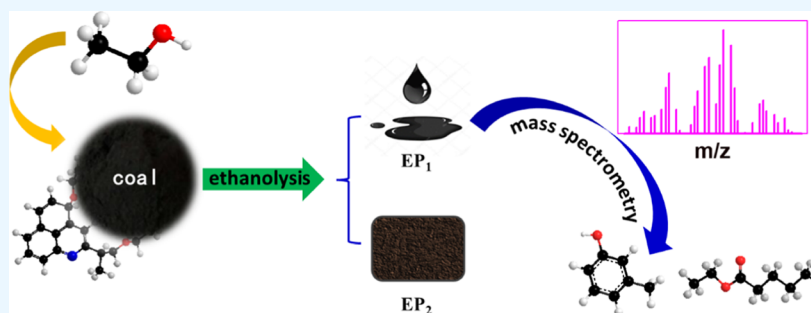
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ABSTRACT: Ethanolsis of lignite is an effective approach for converting organic matter of lignite to liquid coal derivatives. Xilinguole lignite (XL) was reacted with ethanol at 320 °C. Then ethanol and isometric carbon disulfide/acetone mixture were used to extract the reaction mixture in a modified Soxhlet extractor to afford extractable portion 1 (EP₁) and extractable portion 2 (EP₂), respectively. According to analysis of EP₁ with a gas chromatography/mass spectrometer, phenolic compounds made up more than 33% of the compounds detected. This could be ascribed to the ethanolsis of XL; that is, ethanol could selectively break the C_{alkyl}–O bonds in lignite, producing more phenolic compounds. Furthermore, a quadrupole Orbitrap mass spectrometer equipped with an atmospheric pressure chemical ionization source was used for comprehensive analysis of the compositional features of EP₁. The analysis indicated that O_{1–3}, N₁O_{0–2}, and N₂S₁O_{3–6} were predominant class species in EP₁. Nitrogen atoms in NO-containing organic compounds may exist in the form of pyridine or amidogen, while oxygen atoms primarily exist in furan, alkoxy, carbonyl, and ester groups. In addition, possible chemical structures of NO-containing organic compounds were speculated.

1. INTRODUCTION

Lignites are mainly used for nearby combustion and power generation due to the disadvantages of high moisture content, high ash content, easy weathering, and poor thermal stability.^{1,2} However, lignite retains partial structures derived from coal-forming plants, resulting in its high oxygen content. Oxygen atoms in organic matter of lignite exist in the forms of COO[–], C=O, C–O–, and –OH.^{3–6} This natural advantage makes lignite having potential to obtain chemicals. Condensed aromatics containing hetero-atoms are value-added organic chemicals which were used for medicine, pesticides, dyes, and functional materials.^{7,8} Thus, it is of great significance to explore new ways for efficient utilization of lignite.

Supercritical alkanolysis of lignite is an important method to obtain liquid coal derivatives.^{9,10} Low carbon alkanol can effectively destroy the non-covalent association in lignite, which has a good swelling of lignite. Furthermore, alkanol can nucleophilic attack the >C–O–C< in lignite.¹¹ Mondragon¹² speculated that the attack of active free radicals generated by ethanol at high temperature may be the cause of the greater yield of coal derivatives. Lu¹³ investigated the thermal

dissolution behaviors of Hologol lignite in methanol and ethanol at various temperatures, which indicated that 270 and 240 °C were the critical temperatures for methanolysis and ethanolsis of lignite, respectively. Since the nucleophilicity of ethyl is stronger than that of methyl, ethanol can cleave more >C–O–, resulting in higher yields of soluble portions from ethanolsis of lignite than that from methanolysis. Compared with coal pyrolysis, the reaction temperature of ethanolsis of lignite is lower, and most of the products retain the aromatic ring structure.

Supercritical alkanolysis of lignite is an important method to obtain soluble portions. Due to the complex composition of soluble portions, the identifications of the molecular component of its components were facing great challenges. A

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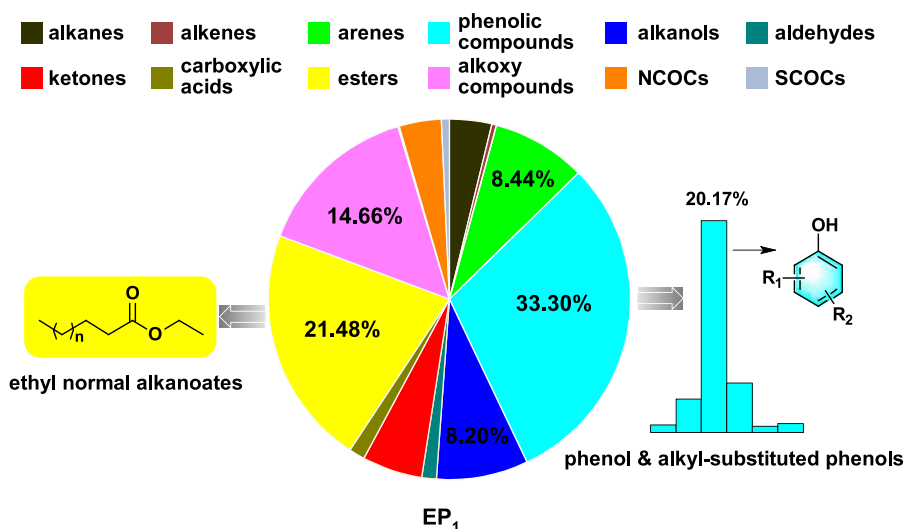


Figure 1. Distribution of group components in EP₁ by GC/MS analysis.

mass spectrometer is an important instrument for analyzing the molecular weight of organic compounds.¹⁴ The combination of a gas chromatograph and mass spectrometer can realize the separation and analysis of organic compounds in coal derivatives with a relative molecular weight less than 500 μ . Our previous study has successfully demonstrated selective destruction of coal and identified the compositional feature of coal derivatives by gas chromatography/mass spectrometry (GC/MS).^{15–17} However, GC/MS was only applicable to analyze volatile and thermally stable organic compounds, which cannot parse out all the compounds in the coal derivatives.

In recent years, development of ionization technologies and high-resolution MS could greatly make up for the shortcomings of GC/MS. New MS techniques have emerged in obtaining more information on the molecular weight of coal derivatives.^{18–20} Quadrupole-Orbitrap MS can accurately determine the molecular formula of organic compounds without chromatographic separation, which possess resolution up to 140,000 at m/z of 200 and a mass accuracy less than 5 ppm. Combined with an atmospheric pressure chemical ionization (APCI) source and Orbitrap MS, the molecular formula of compounds can be well detected, especially those containing O, N, and S atoms.^{21,22} In addition, lignite derivatives contain a large number of heteroatomic compounds. The study of these heteroatomic compounds by high-resolution MS will promote the understanding and utilization of compounds obtained from the lignite soluble portion.

In this investigation, Xilinguole lignite (XL) was subjected to ethanolysis at 320 °C for obtaining soluble portions which were subsequently analyzed with two mass spectrometers. The compositional features of lignite derivatives will provide a theoretical basis for the subsequent separation of value-added coal-based chemicals.

2. EXPERIMENTAL SECTION

2.1. Coal Samples and Reagents.

XL was acquired from Xilinguole, Inner Mongolia, China. The proximate and ultimate analyses of XL are reported in the previous literature.¹⁰ The XL sample was dried at 80 °C for 24 h in a vacuum oven after crushing into a powder below 200-mesh before reaction with ethanol. All the reagents, such as ethanol,

acetone, and carbon disulfide (CDS), employed in the experiment were distilled before use.

2.2. Ethanolysis of XL.

A 100 mL magnetically stirred autoclave was used for the ethanolysis of XL, and 2 g of XL was placed into it with 20 mL of ethanol. The equipment was heated to 320 °C and remained for 2 h after swapping out air with nitrogen three times. Then the reaction mixture was transferred to a modified Soxhlet extractor after cooling to room temperature. 150 mL of ethanol and isometric CDS/acetone were added into the extractor for extracting organic soluble components. Each extraction was proceeded 48 h at reflux temperatures to provide extractable portion 1 (EP₁) and extractable portion 2 (EP₂). The yield of each EP was computed as $Y = m_{EP}/m_{XL,daf}$ where m_{EP} is the mass of the EP and $m_{XL,daf}$ is the mass of the XL on a dry and ash-free basis. The ethanolysis of lignite and subsequent extractions were repeated three times. The yields of EPs were the average of three experiments, and the errors for the yields are less than 3%.

2.3. Analyzing EP with GC/MS and Quadrupole-Orbitrap MS.

The EPs were analyzed with an Agilent 7890/5975 GC/MS and a Thermo Scientific Q Exactive quadrupole-Orbitrap MS coupled with an APCI source. The instrument parameters were described previously.¹⁰ The temperature program of GC/MS was set as 3 °C·min⁻¹ from 60 to 300 °C and maintained for 6 min. The main parameters for the APCI source including discharge current, capillary temperature, and vaporizer temperature were set at 4.0 μ A, 275, and 300 °C, respectively. The GC/MS data analysis was performed on ChemStation software with NIST11 library. TraceFinder 3.0 was applied for identification, confirmation, and quantification analysis of quadrupole-Orbitrap MS data cooperated with Microsoft Excel 2010. Relative intensity, m/z , errors, double bond equivalent (DBE), and composition were exported in an Excel table. The data with the errors less than 3 ppm were selected. Then a self-programmed program was executed by macro instruction for sorting the compositions.

3. RESULTS AND DISCUSSION

3.1. Yields of EPs.

A large amount of organic matter would be released in thermal dissolution of coal. The yields of EPs obtained from XL ethanolysis at 320 °C are 37.7 and 20.7 wt %

Table 1. Ethyl Esters Detected in EP₁ with GC/MS

peak	compound	RA (%)
8	ethyl 3-methylpentanoate	0.198
11	ethyl hexanoate	2.913
12	ethyl hex-4-enoate	0.870
13	ethyl hex-3-enoate	2.285
16	ethyl hex-2-enoate	5.772
24	ethyl heptanoate	0.568
25	ethyl 2-ethylhexanoate	0.481
28	ethyl octanoate	0.331
32	ethyl 3-cyclohexylpropanoate	0.288
34	ethyl benzoate	0.308
37	ethyl octanoate	1.531
38	ethyl oct-3-enoate	0.729
44	ethyl oct-2-enoate	1.391
45	ethyl 2-methylbenzoate	0.222
50	ethyl nonanoate	0.375
62	ethyl decanoate	0.790
94, 119 & 122	ethyl tridecanoate	0.261, 0.067 & 0.081
101	ethyl 1,1-dimethyl-2,3-dihydro-indene-4-carboxylate	0.612
107 & 124	ethyl palmitate	0.126 & 0.073
113 & 128	ethyl stearate	0.147 & 0.219
127 & 129	ethyl tetracosanoate	0.305 & 0.532

(daf), respectively, which are much higher than that from thermal dissociation with methanol.¹⁰ After the two-step extraction of the ethanolysis reaction mixture, 58.4% organic matter in XL was released to EPs. This means that ethanol is an effective solvent to obtain organic matter from XL under supercritical conditions.

3.2. Molecular Compositions of the EP₁ Analyzed with GC/MS. Analyzing with GC/MS, 129 organic compounds in EP₁ were detected, which are listed in Tables S1–S12. All the compounds were systematized into normal alkanes, alkenes, arenes, phenolic compounds, alkanols, aldehydes, ketones, carboxylic acids, esters, alkoxy compounds, nitrogen-containing organic compounds (NCOs), and sulfur-containing organic compounds (SCOCs).

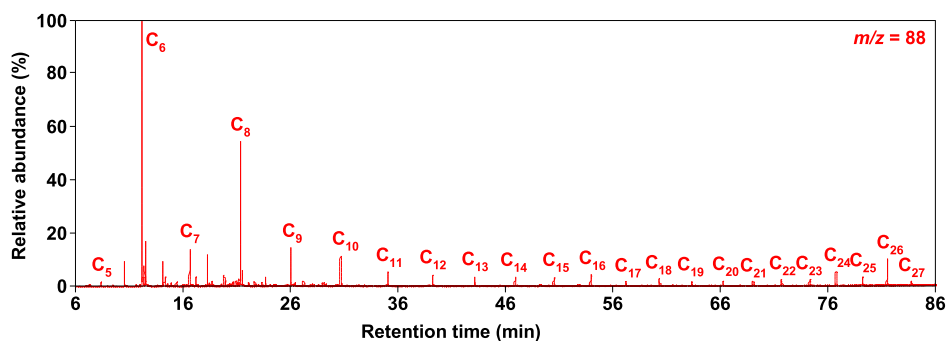
As shown in Figure 1, phenolic compounds make up 33.30% of the compounds detected in EP₁, and 20.17% phenolic compounds were phenol substituted with two alkyls. A possible reason for high content of phenolic compounds could be the ethanolysis of XL; that is, ethanol can selectively cleave the C_{alkyl}–O, C_{acyl}–O, and/or C_{aryl}–O bridged bonds, producing

more phenolic compounds.¹³ Furthermore, the dissociation of methoxy group in guaiacols²³ and alkylation reaction of phenols^{24,25} produce the higher relative content of alkyl-substituted phenols. It will be an important strategy to produce phenolic compounds from ethanolysis of lignite since phenols are an important chemical raw material.

As shown in Table 1, 21 ethyl alkanates were found in EP₁, accounting for 21.48%. It was found that all the mass spectrograms of ethyl alkanates contained base peaks *m/z* = 88. As displayed in Figure 2, the selective ion chromatogram of *m/z* = 88 was analyzed, in which the carbon number of ethyl alkanates was mainly concentrated in C₅–C₂₇. According to literature reports, there is a large amount of methyl alkanates in the EPs from methanolysis of lignite,¹¹ which is attributed to esterification or transesterification reaction. On one hand, it can be inferred that the ethyl alkanates are derived from the esterification reaction between alkanic acid in lignite and ethanol. On the other hand, alkanates are linked to the large skeleton structure of lignite. The oxygen atom in ethanol is relatively electronegative, preferring to attack the carbon atom linked to the oxygen atom, which is highly electronegative. As a result, the C–O bond is activated, resulting in further fracture, and the straight chain alkanate compound is generated.

3.3. Molecular Mass and Class Distribution of Compounds Detected with Orbitrap MS in EP₁. Orbitrap MS equipped with an APCI source has proved to be a practical instrument for determining the molecular weight distribution of soluble coal derivatives.^{26,27} An APCI source is suitable for the detection of medium-polarity and volatile compounds. As shown in Figure 3, although the molecular masses of EP₁ exhibit nearly normal distribution in both positive ion mode and negative ion mode APCI sources, compounds were easily ionized in the positive ion mode APCI source. Moreover, the molecular mass distribution of EP₁ analyzed in the positive ion mode APCI source is different from that in the negative ion mode APCI source. As shown in Figure 3, the molecular masses of compounds analyzed in EP₁ mainly concentrate on 150 to 450 *u* in the positive ion mode APCI source, while the range is from 200 to 500 *u* in the negative ion mode APCI source.

The DBE can be calculated from the molecular formula, which reflects the condensation degree of compounds.²⁸ As clarified in Figure S4, DBE values of the compound detected in EP₁ with the positive ion mode APCI source were concentrated in 0–7, while the values were widely scattered under the negative ion mode APCI source. EP₁ was analyzed with a Q-OMS under positive ion mode APCI and negative ion mode APCI sources and classed into O_{0–6}N_{0–2}S_{0–2}. As

**Figure 2.** Selective ion chromatogram of ethyl alkanates in EP₁.

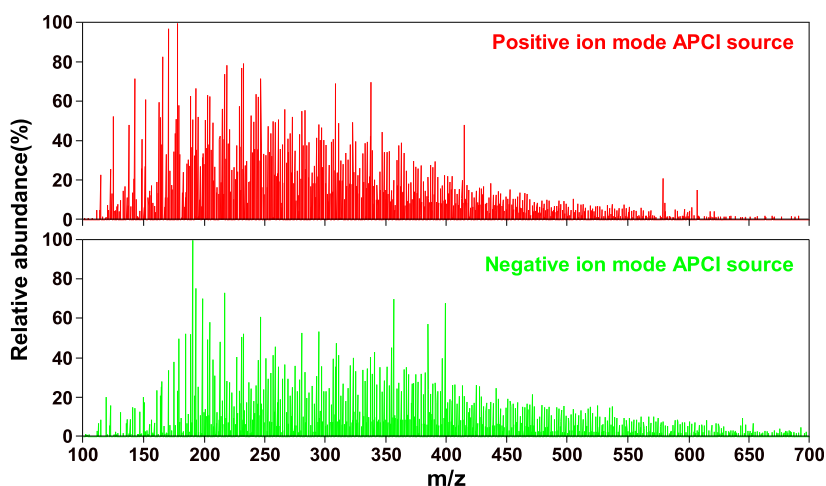


Figure 3. Broadband mass spectra of EP₁ from analysis with Orbitrap MS in both positive ion mode and negative ion mode APCI sources.

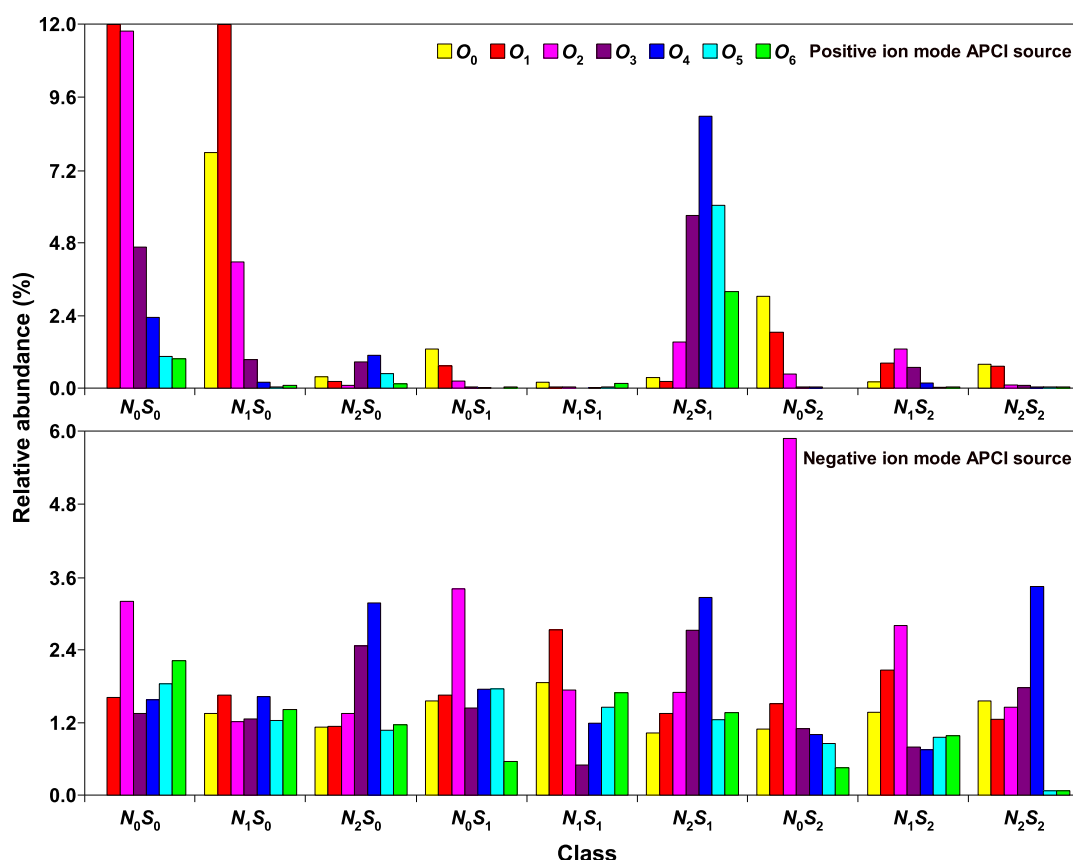


Figure 4. Distributions of O_xN_yS_z group components in EP₁ from analysis with Orbitrap MS in both positive ion mode and negative ion mode APCI sources.

exhibited in Figure 4, O₁₋₃, N₁O₀₋₂, and N₂S₁O₃₋₆ group components recognized under the positive ion mode APCI source are prominent in EP₁, while S₂O₂ is the primary component identified with the negative ion mode APCI source.

3.4. O_x and N₁O_x Components Detected with Orbitrap MS in EP₁. As shown in Figure 5, the distributions of O₁₋₃ components were similar, while O₄₋₆ components have a scattered distribution. The O₁₋₃ species mainly concentrated in carbon numbers of 7–24 and DBEs of 3–7 under the positive ion mode APCI source, implying that most compounds

contain two aromatic rings. Previous studies²⁹ have shown that oxygen atoms in soluble coal derivatives may emerge in phenols, alkoxy groups, furans, acids, esters, and ketones. Therefore, the O₁ component with DBE values of 3 and 6 could be attributed to alkyl furan and alkyl benzofuran, respectively. The O₁ components with DBE = 4 are most likely to be alkoxy benzene since alkoxy groups widely existed in lignite. Aromatic ketones could be the primary O₁ component with DBE = 5. Meanwhile, most of the O₂₋₆ components contain one or more ester groups. The O₂₋₃ components with DBE = 5 and O₄₋₅ components were speculated to alkyl

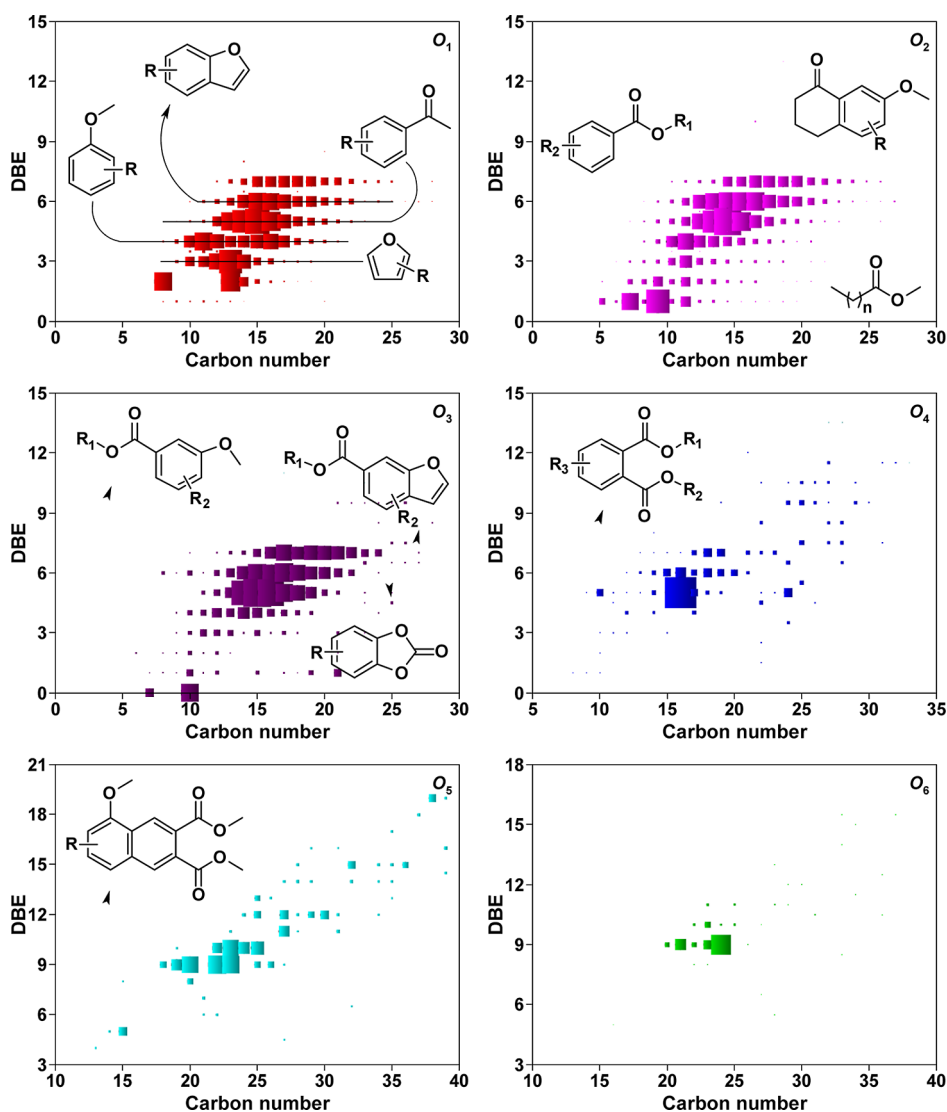


Figure 5. Iso-abundance plots of DBE vs carbon number for the O_x group components from analysis with Orbitrap MS in the positive ion mode APCI source in EP_1 .

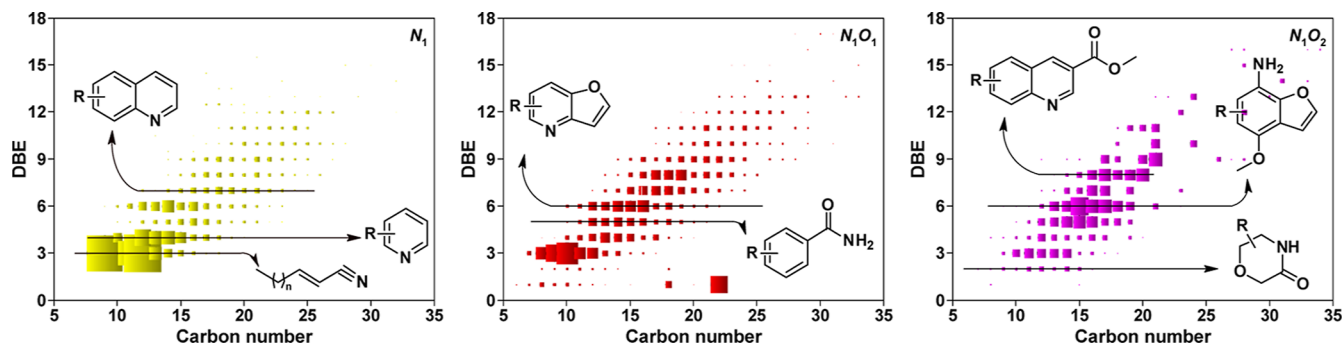


Figure 6. Iso-abundance plots of DBE vs carbon number for the N_1O_{0-2} group components from analysis with Orbitrap MS in the positive ion mode APCI source in EP_1 .

benzoate and alkyl phthalate, respectively. The analysis result is consistent with that from GC/MS.

High-resolution MS^{30,31} is effective for studying the occurrence of nitrogen in soluble coal derivatives. The nitrogen atom in pyridine could be ionized in the positive ion mode APCI source. N_1 , N_1O_1 , and N_1O_2 components were concluded, in which N_1O_1 component was the most abundant

group component. As displayed in Figure 6, the N_1 components with the DBE values of 4 and 7 are probably alkylpyridine and alkylquinoline, respectively. The N_1O_1 component widely distributes in carbon numbers of 7–29 and DBEs of 3–9. The N_1O_2 components with DBE values of 5 and 6 were speculated to be furopyridines and benzamides, respectively. Analyzing with GC/MS, phenols, alkanols,

aldehydes, ketones, carboxylic acids, esters, and alkoxy compounds were identified in EPs. The oxygen atom in N_1O_2 component may appear in alkoxy, ester, or carbonyl group. Hence, the N_1O_2 component could be ascribed to alkylquinoline or alkylfuropyridine-substituted methoxy and/or ester group. The reason for generating high content of N_1O_x components is the nucleophilic attack of ethanol resulting in the cleavage of C–O bond between nitrogen-containing rings and macromolecular groups in lignite.¹¹

4. CONCLUSIONS

In total, more than 58.4% organic matter in XL was released to SPs after ethanolysis of XL at 320 °C. According to GC/MS analysis, 33.3% phenols and 21.48% ethyl alkanates were detected in EP₁, which could be a potential strategy to produce oxygen-containing compounds from ethanolysis of lignite. Meanwhile, O_{1-3} , N_1O_{0-2} , and $N_2S_1O_{3-6}$ group components identified in the positive ion mode APCI source were predominant in EP₁, and the chemical structures were speculated. The oxygen atoms in O_{1-3} group components mainly exist in furan, alkoxy, carbonyl, and ester groups, while nitrogen atoms primarily exist in pyridine and amidogen.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.2c05051>.

Instrument parameters and analysis conditions of analyzing EP with GC/MS and quadrupole-Orbitrap MS; total ion chromatogram of EP₁; molecular mass and DBE distribution of the species identified in EP₁ with Orbitrap MS in both positive ion mode and negative ion mode APCI sources; and list of compounds detected in EP₁ with GC/MS (PDF)

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Notes

The authors declare no competing financial interest.

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■ NOMENCLATURE

APCI	atmospheric pressure chemical ionization
CDS	carbon disulfide
DBE	double bond equivalent
EPs	extractable portions
EP ₁	extractable portion 1
EP ₂	extractable portion 2
GC/MS	gas chromatography/mass spectrometry
NCOCs	nitrogen-containing organic compounds
Orbitrap MS	Orbitrap mass spectrometer
RA	relative abundance
SCOCs	sulfur-containing organic compounds
XL	Xilinguole lignite

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