



Soluble Organic Matter Affecting Low-Temperature Oxidation of Coal with Different Ranks

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Soluble organic matters in three different ranks of coal were extracted by the tetrahydrofuran. After treatment the product ingredients in the extract and microstructure change at the coal surface were measured. During the process of heating, the emissions released from the coal before and after extraction also be considered as indicators for evaluating the role played by the soluble organic matters. The results show that the extracts mainly contain aromatic and oxygenated compounds. It is noted that the active groups in the residual coal significantly reduced compared to the raw coal. By contrast, the total pore-volume and specific surface-area in the residual coal grow in varying degrees. Especially, the lower the coal rank is, the more obvious these variations are. In the procedure of low-temperature oxidation, the oxygen consumptions of residual coal with different rank all decrease. Regarding the soft coal and coking coal, the emissions of CO, CO₂, C₂H₄ and C₂H₆ also decline. However, for the anthracite, the emissions of CO₂ and C₂H₆ increase at the temperature from 110-130 °C. Further, the apparent activation energy of soft coal, coking coal and anthracite boosts after the extracted processing, which suggested that the existence of soluble organic matters is propitious to the occurring of spontaneous combustion of coal.

Keywords: Coal, Soluble organic matters, Coal rank, Active groups, Low-temperature oxidation.

INTRODUCTION

As a kind of organic rock, the coal involves plenty of small molecules and soluble organic matters (SOMs) in its network structure. These SOMs mainly consist of aliphatic hydrocarbons, aromatic and heteroatom-containing compounds, which occupying 1 to 30 % content in the coal¹⁻⁴. The spontaneous combustion of coal, a dynamic alteration, is affected by mutual influence and combined effects of internal and external factors. Previous studies have indicated that the self-ignite of coal is essentially caused by the heat accumulation stemmed from the oxidation of active groups, whereas the oxygen-supply conditions depend on the pore structure⁵. Therefore, The pore structure and active groups of coal directly determine the sensitivity of coal reacting with oxygen. Tion *et al.*⁶⁻⁸ investigated the chemical speciation and composition of SOMs in the coal and found that these SOMs includes a wide range of hydrocarbons, for instance, from C1 to C30. Chen *et al.*⁹ reported that the pore volume of coal increases obviously after the dissolution of free or embedded organics in the structure of polymer network. More importantly, after the handling, pore channels were dredged and the pore structures were gradually simplified. In fact, that there is a close connection among the SOMs, pore structures and active groups in the coal. Thus, the self-heating of coal may also be impacted by

mentioned relationships. However, the role of SOMs plays in the low-temperature oxidation of coal has yet to be defined. It is necessary to uncover this issue because of this research result is expected to provide a reference for evaluating the potential heat hazard in coal-related industries.

In this paper, the conjunctive using of GC/MS and FTIR not only revealed the microstructure change of coal, also tested the products in the extracts after the infiltration of tetrahydrofuran. The variation of pore structure was studied according to methods of the BJH and BET. The additional data of gases emissions obtained from the temperature-programmed experiments corroborate the results sufficiently as well.

EXPERIMENTAL

Three different grades of coal, Qingdong coking coal (QD No. 8), Guobei soft coal (GB No. 8) and Anyang anthracite (AY No. 2), were selected for the experimental samples. Fresh coal samples were collected and sealed in the underground colliery at first and then were transported back to the laboratory. After the treatment of stripping, breaking and screening, the coal samples (0.180-0.250 mm) were prepared. The maceral and technical parameters of coal are shown in the Table-1.

The extraction experiments were conducted by the CW-2008 multi-microwave reaction/extraction device, Zeming Tech Co., Ltd.. The detail procedures are as follows: Firstly,

TABLE -1
ANALYSES OF COALS AND EXTRACTION WITH THF SOLVENT

Coal sample	Proximate analysis (wt.%, daf)			R _v , max %	Vitrinite Mmf. %	Liptinite Mmf. %	Extraction yield (wt. %, daf) (THF)
	VM	ash	FC				
QD No.8	29.34	24.17	66.49	0.93	46.2	46.1	2.531
GB No.8	17.37	20.06	62.59	1.46	62.1	37.9	2.169
AY No.2	9.11	19.55	71.34	2.64	55.4	44.6	0.742

take 50 g of coal samples and 300 mL THF solvent (AR) to mixture into the reaction vessel. After the microwave-assisted extraction (0.5 h) under the ambient pressure at 30 °C, the extract and residual coal were separated by filtration. Moreover, the residual coal was further dried in vacuum (12 h). The extraction rate of coal samples is shown in Table-1.

The FTIR experiments were tested by the Nicolet Avatar 360-type infrared spectrometer, Thermo Fisher Scientific (China) Co Ltd. The IR spectral range from 4000-400 cm⁻¹ was collected and each coal sample was scanned 32 times. The pore-structure parameters of coal were measured *via* the method of low-temperature nitrogen adsorption. After vacuum degassing, coal sample (1 g) was tested by the ASAP 2020 type surface area and porosimetry analyzer (Micromeritics Instrument Corporation) before and after extracted processing, respectively. Under the condition of 77K and the relative pressure from 0.009 to 0.998, twenty-four pressure points were marked and the nitrogen adsorption of each point was calculated separately. The ingredients of extracted products were tested by the GC/MS (HP6890/5973 type, HP Co. Ltd). In terms of testing on the low-temperature oxidation of coal, gases products were defined by the SP-50N1 gas chromatograph (East & West Analytical Instruments Co. Ltd.)

RESULTS AND DISCUSSION

The infrared spectra of raw coal and residual coal was shown in Fig. 1. According to the Fig. 1, three kinds of coal samples have the similar peak positions and peak shapes, but different in peak height.

The absorbances in 3684-3625, 3624-3610, 1690-1660, 1330-1110 and 1110 cm⁻¹ are appeared in the soft coal, coking coal and anthracite. For all three kinds coal, relative content of major functional groups in raw coal was significantly higher than that in extracted coal. Only in the anthracite, the hydroxyl associated with the hydrogen and stretching vibration of Ar-O-C were increased after extraction. Obviously, the SOMs in coal contain large amounts of oxygen-containing reactive-groups. But, changes of the oxygen functional groups in the coal gradually decreased with the growth of coal rank, which indicated that the SOMs in the anthracite contained less oxygen-reactive-groups than that in the low rank coal.

Absorption peaks at 3056-3032 cm⁻¹ (-CH), 1605-1595 cm⁻¹ (Stretching vibration of C=C), 900-850, 825-800 and 770-730 cm⁻¹ represent the aromatic rings and related structures in coal molecules. After extraction, contents of mentioned structures have dropped significantly to the soft coal and coking coal. However, as the anthracite, aromatic hydrocarbons essentially remain stable.

This phenomenon also occurs in the changes of the aliphatic hydrocarbons. Aliphatic hydrocarbons, including the peaks shown in 2935-2915 cm⁻¹ (asymmetric stretching of

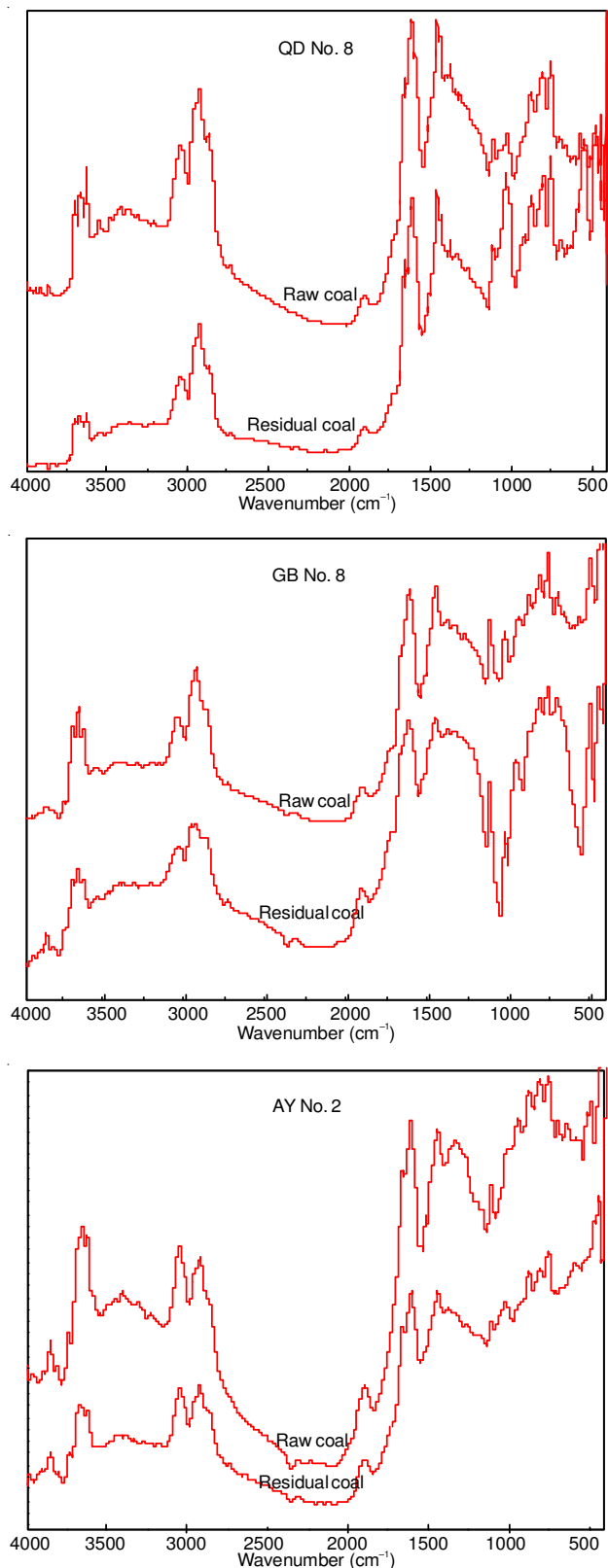


Fig.1. Infrared spectra of raw coal and residual coal

CH₂), 2857-2851 cm⁻¹ (symmetric stretching of CH₂), 1460-1435 cm⁻¹ (antisymmetric deformation vibration of CH₃) and 1384-1367 cm⁻¹ (scissoring vibration of CH₃), are dramatically reduced in the soft coal and coking coal. Interestingly, instead of reduction, the content of aliphatic hydrocarbons keeps unchanged and even slightly increases in the anthracite. This result suggests that, owing to the breaking of partial non-chemical bonds, some structures in the aliphatic hydrocarbons have dissolved in the THF since the occurrence of extraction. Meantime, minerals, such as 1031 cm⁻¹ (stretching vibration of Si-O-Si or Si-O-C), 540 cm⁻¹ (S-S) and 495 cm⁻¹ (-SH), are weakened or even vanished in the coal in the light of spectra.

Overall, the total contents of functional groups in all three coal samples decline considerably, which indicate that the SOMs occupy a large proportion to the coal. The residual coal will have a greater transmutation in the course of low-temperature oxidation, due to the changing of its own compositions. Specifically, absorptions at the 3690 and 3616 cm⁻¹ (oxygen-containing groups) still have strong peaks in the GB residual coal. For the QD coal sample, the peaks keep powerful at 1440 and 1380 cm⁻¹ (Aliphatic hydrocarbon), but drop in 3040 cm⁻¹ (aromatic hydrocarbon). By contrast, the functional groups of anthracite are lower at all spectral peaks. After the treating, the decrement order of functional groups for three coal samples is as follows: soft coal > coking coal > anthracite. This phenomenon may be because low rank coals generally contain abundant SOMs, activity groups and side chains¹⁰. In addition, with the growing of metamorphism reaction, polycondensation of aromatic nucleus in the coal increases and reactive groups and side chains both decrease.

Pore structure: According to the BET and BJH methods, the specific surface area, pore volume, average pore diameter of coal are shown in Table-2 and the distribution of pore volume is shown in Fig. 2.

Table-2 shows that the pore volume and specific surface area of the residual coal increase obviously. The data of GB have a maximum increase because higher content of SOMs in this coal. Fig. 2 illustrates that the number of holes which diameter range 5-10 nm markedly increased. And after extraction, the average pore size of soft coal decreases evidently, as well as the coking coal. On account of small organic molecules are dissolved, the expanding and dredging of pore are happened in the coal. As the result, the specific surface area and total pore volume increase following the change of pore structure in the coal, which consistent with the conclusions of previous studies^{11,12}.

GC/MS analysis: Fig. 3 represents the chromatograms of THF extracted from three coal samples.

It can be seen clearly that there are 41 and 17 kinds of substances detected in the extracts of QD and GB. In compa-

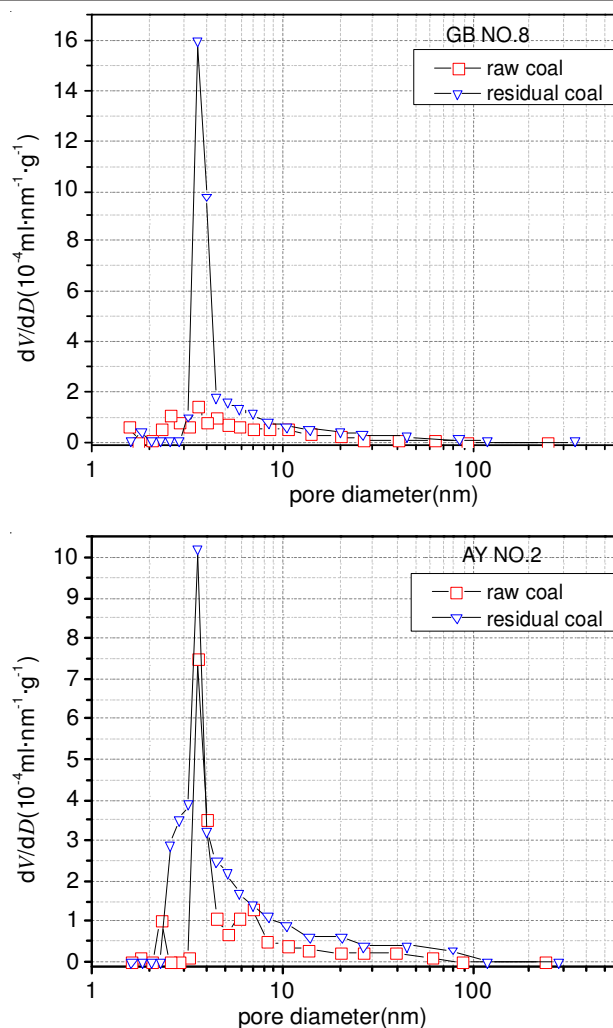


Fig. 2. Distribution of pore volume for two kinds of coal samples

risson, only 7 kinds of matters are found among the extracts of AY, which further reflect that the high-rank coal has fewer amount and type small-organic-molecules. This outcome corresponds well with the data of extraction rate shown in Table-2. Matters, such as *p*-xylene(QD 1# peak), styrene (QD 2# peak), butyrolactone(QD 3# peak), diphenylmethane (QD 13# peak), 2,6-di-*tert*-butylcyclohexa-2,5-diene-1,4-dione (QD 15# peak),

(2*a*S,2*a*¹S,4*a*R,7*a*S)-2*a*,3,4*a*,7*a*-tetramethyl-2,2*a*,4*a*,5,6,7*a*-hexahydro-1*H*-cyclopenta[*cd*]inden-7(2*a*1*H*)-one (QD 16# peak) are emerged at all three kinds of extracts. Apart from these matters, 4-(*tert*-butyl)-2,6-diisopropylphenyl acetate (QD 14# peak), 4,4'-(ethane-1,2-diyl)*bis*(2,6-di-*tert*-butylphenol) (QD 33# peak) both show in the spectrogram of QD. At the same time, GB has considerable content of *bis*(2-ethylhexyl) decanedioate (GB 13# peak).

TABLE-2
PORE VOLUME AND SPECIFIC SURFACE AREA OF COAL

Coal sample		Average pore size d/(nm)	Pore volume v/(cm ³ g ⁻¹)	Total specific surface A/(m ² g ⁻¹)
GB NO. 8	raw coal	13.26	0.0019	0.3265
	residual coal	11.19	0.0054	0.6886
AY NO. 2	raw coal	11.05	0.0029	1.5099
	residual coal	10.65	0.0078	1.6356

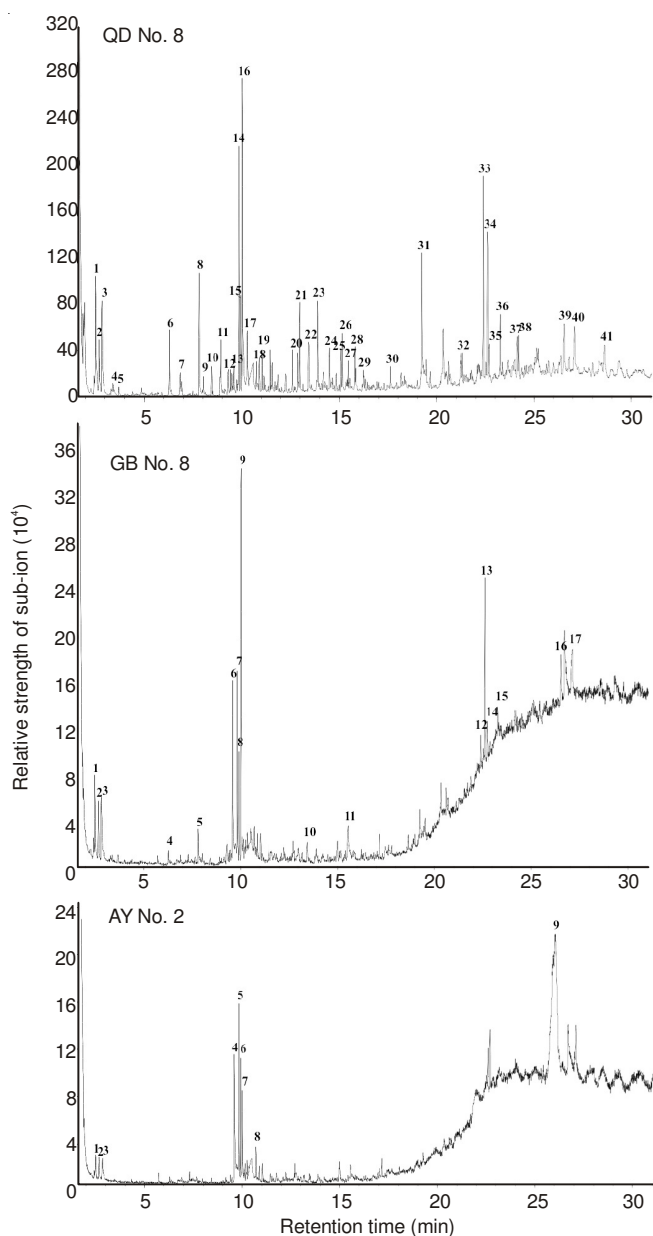


Fig. 3. Chromatograms for compositions of extracts

The extracts of low rank coals (QD and GB) contain large number and variety of active groups. And SOMs include abundant structures, for instance the methyl, hydroxyl, carbonyl and ester, *etc.*

Gas emission: Indicators like O_2 consumption or emission of CO , CO_2 and C_xH_y are directly related to low-temperature oxidation of coal. The measurement of such indicators can characterize the strength of low-temperature oxidation of coal. For studying the SOMs in the coal effect on the low-temperature oxidation of coal, oxygen consumption and gaseous products emission before and after the extraction are tested.

Fig. 4 shows trends of O_2 consumption varying with temperature during the low-temperature of raw coal and residual coal.

Oxygen consumption rate of all three ranks coals exponentially growing with the growth of temperature. From the beginning to the end, the data of raw coal always are higher than that of residual coal. In the initial stage ($< 70^\circ C$), there is

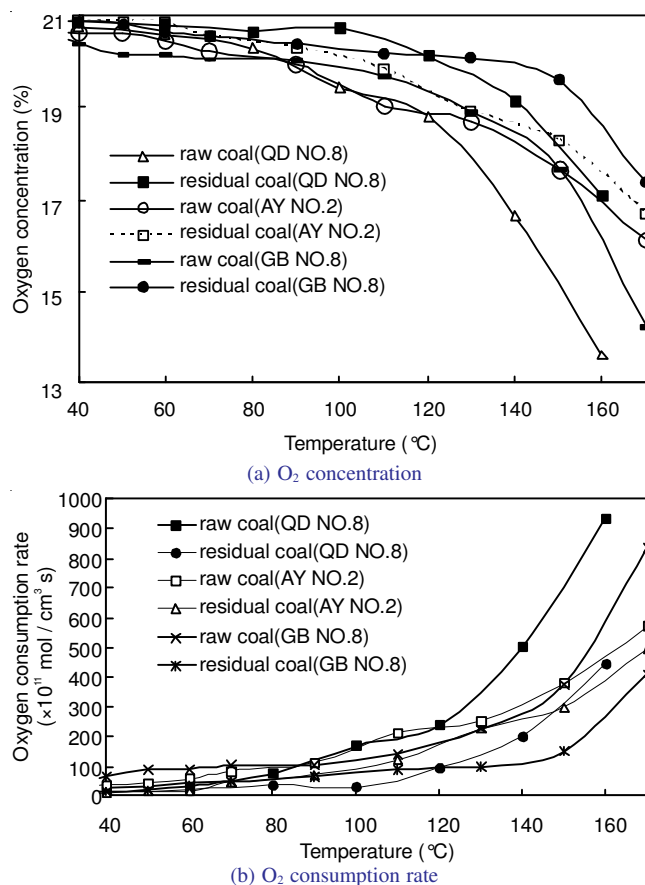


Fig. 4. Oxygen consumption of raw coal and residual coal

only little difference between the two group data. The increasing trend of data in raw coal rapid rises after the temperature over $70^\circ C$. The difference of oxygen consumption rate between raw coal and extracted coal has inverse relationship with the metamorphic grade of coal. For example, the Anyang anthracite has little change in oxygen consumption rate before and after extraction.

The CO , CO_2 , CH_4 , C_2H_6 and C_2H_4 emission varies with temperature were revealed in Fig. 5-9.

For the QD and GB, the emission of CO and CO_2 is arisen until the temperature climbed to $40^\circ C$ and $50-60^\circ C$, respectively. And then it gradually increases with the rising of temperature. Throughout the process, data of residual coal are always higher than that of raw coal. There is an exceptional case for AY, before $110^\circ C$, the CO and CO_2 released from raw coal are slightly larger than that from residual coal. However, the situation is completely reversed after $110^\circ C$. Combined with the spectral analysis of AY coal sample, alcoholic and phenolic hydroxyl groups in the AY anthracite are enhanced after the extracted processing. Under oxidation effects, these oxygen-containing groups are directly generated carbonyl structures, which provide additional sources for CO and CO_2 .

Similarly, the alkane gases have an increasing trend with the temperature rising. Using GB coal as the example, at $170^\circ C$, the CH_4 , C_2H_4 and C_2H_6 concentration produced by the raw coal is 40.21, 3.27 and 57.7 ppm, respectively. With the hysteresis generating, the data of residual coal are 11.59, 1.60 and 8.36 ppm at $170^\circ C$, respectively. Strangely, contrary to the GB and QD coal, the AY anthracite has more complex

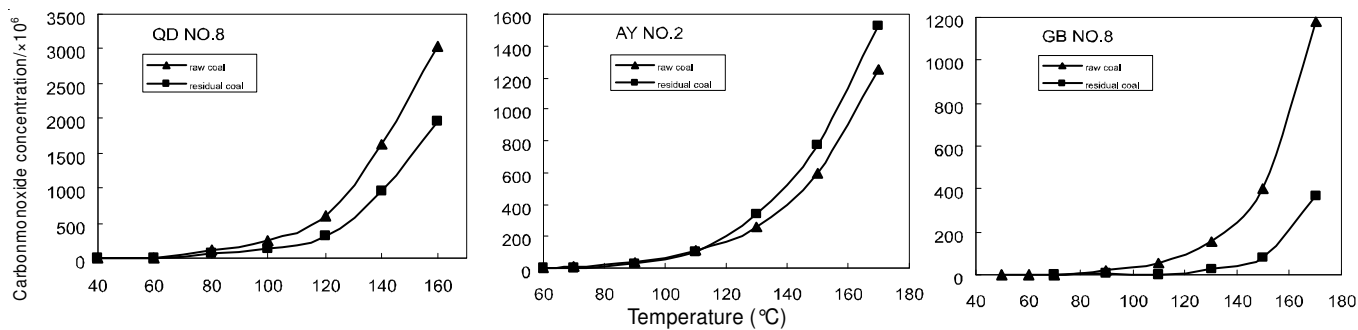


Fig. 5. CO concentration change with temperature

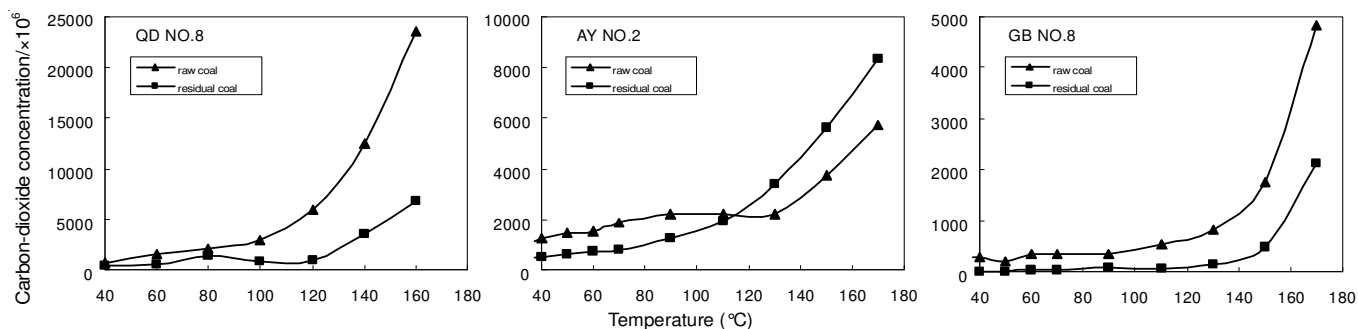


Fig. 6. CO₂ concentration change with temperature

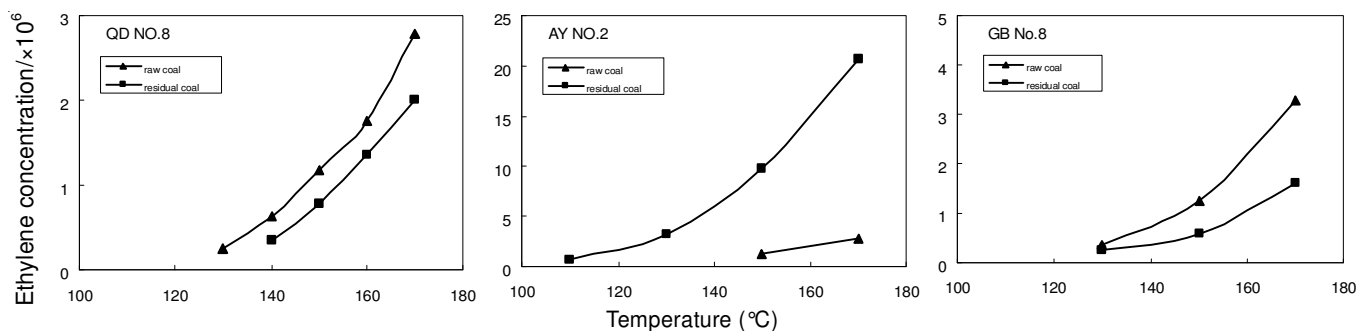


Fig. 7. CH₄ concentration change with temperature

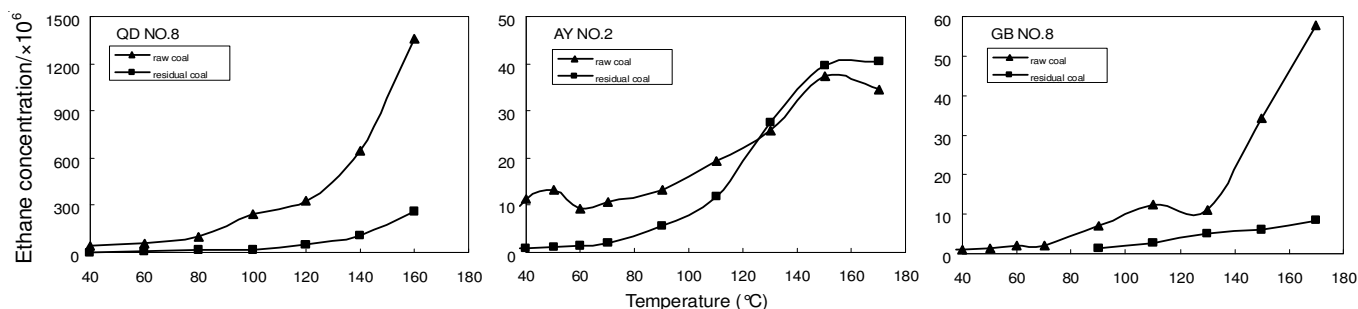


Fig. 8. C₂H₆ concentration change with temperature

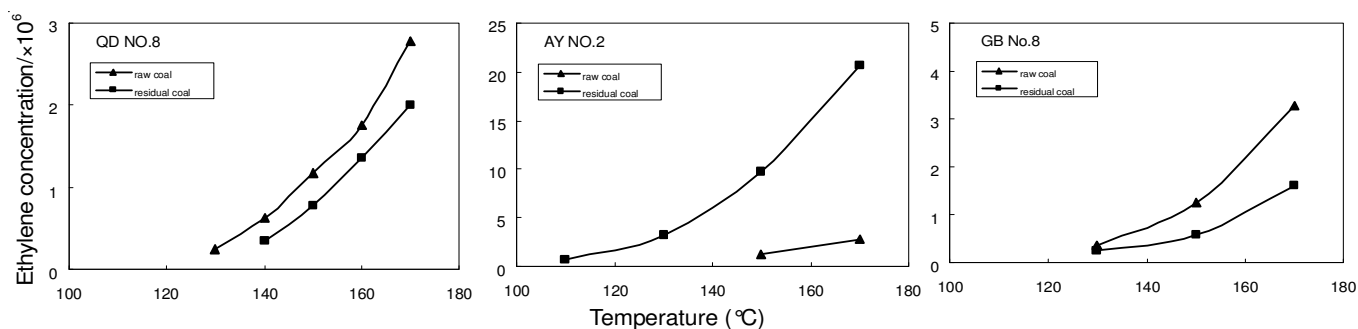


Fig. 9. C₂H₄ concentration change with temperature

variation in emission of CH₄, C₂H₄ and C₂H₆. The residual coal has higher yields in C₂H₄, while has lower yields in CH₄ than the raw coal. Initially, the C₂H₆ production of raw coal is higher than the number of residual coal until 130 °C, but then has an opposite trend. It can be believed that in the AY anthracite, the multiple variations affected by the THF are responsible for the previous results.

Mechanism: Based on the properties of gas emission, the raw coal has higher tendency of self-heating and more susceptible to occur spontaneous combustion than the residual coal extracted by the THF. For the same coal, the intensity of low-temperature oxidation relies on the number of reactive groups, mineral content and the specific surface area in the coal¹³. Therefore, active groups and pore characteristics directly demonstrate oxidation properties of the coal.

After extracted treatment, a series of changes occurred in coal. In the low rank coal, the hydroxyl, carboxyl, some branched chain of aliphatic hydrocarbons and oxygen-containing functional groups all decreased, but the polycyclic increased. Whereas, the hydroxyl-C, carboxyl-C and oxygen-containing functional groups went up instead of down and aliphatic and aromatic hydrocarbons declined. To be sure, with strong antioxidant capacity and aromatization degree, three kinds of extracted coal samples entirely have more oxygen content and fewer active side chains, which cause them hard to react with oxygen^{14,15}, then resulting them consume less oxygen than the raw coal.

The content of minerals in the coal, including S, Fe, Mn, Cu, Zn, P and other elements¹⁶, was dropped significantly after handling. Particularly, total content of minerals in QD coal was declined from 7.535 m²/g to 0.378 m²/g, while the S-S even absents absolutely. It's well known that the reduction of Fe²⁺ and S will inhibit oxidation. Meanwhile, minerals in coal can be bound to organic groups as the carboxyl group (-COOH), phenolic hydroxyl group (-OH), mercapto group (-SH) and imino (=NH), *etc.* Sequentially, low-temperature oxidation of coal is accelerated by these minerals¹⁷.

The SOMs in coal are dissolved and total pore volume and surface area increased in varying degrees, in particular, the number of micropores rose substantially. Pores are dredged owing to the enlarging and expanding effects. High porosity in internal structure of residual coal causes the large amount of free space existing at the surface and inside of coal particles. Even the increase in the specific surface area of coal will promote oxidation, the depletion of active groups and minerals will suppress the self-ignite of coal. For the low rank coal like QD and GB, active substances dominant the oxidizing intensity of coal. In contrast, effects by the porosity play a greater role in the AY anthracite.

According to test results obtained from rate of oxygen consumption, the apparent activation energy of QD, AY and GB coal samples is 33.71, 30.84 and 21.74 kJ/mol, respectively. The corresponding data of residual coal are 38.41, 34.47 and 26.51 kJ/mol, respectively. Obviously, the energy required for the activation reaction is decreased because the presence of SOMs. Thereby, the spontaneous combustion of coal is more susceptible to happen^{16,17}.

Conclusion

In summary, the microscopic structures changed at the surface of extracted coal are as follows: The content of hydroxyl-C, carboxyl-C, branched chain (aliphatic hydrocarbon) and oxygen functional groups all decreased. The number of fused rings increases and the side chains with rich oxygen decrease, which make the coal structure more stable. The extracts mainly consist with the aromatic compounds and benzene oxygenates. Number of methyl, hydroxyl, carbonyl, ether and other active groups are detected in the SOMs in the coal.

Total pore volume and specific surface area of the residual coal increased in varying degrees compared to the raw coal. The rate of increase is inversely proportional to the coal rank. The SOMs mainly occur in the pore range 5-10 nm for the number of holes with these diameters increased significantly after the extracted process.

During the experiment of programmed heating, compared to the raw coal, the oxygen consumption of extracted coal decreased. The CO, CO₂, C₂H₄ and C₂H₆ generated by the oxidation of soft and coking coal all declined. However, the anthracite has a complicated trend in CO₂ and C₂H₆ emission. Before the 110-130 °C, the production of CO₂ and C₂H₆ from the raw coal is larger than the data of residual coal, but this situation transposed once the temperature reaches 110-130 °C.

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