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Study on coal pyrolysis characteristics by combining different pyrolysis reactors

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ABSTRACT

The pyrolysis process of Shendong coal (SD) was first studied by combining the characteristics of thermal gravimetric (TG), pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) and Gray-King assay (G-K). The results show that the order of coke yields is G-K (76.35% (mass))>TG (73.11% (mass))>Py (70.03% (mass)). G-K coke yield caused by condensation reaction and secondary reaction accounts for 3.08% (mass) and 3.24% (mass), respectively. Compared with slow pyrolysis, fast pyrolysis has stronger fracture ability to coal molecules and can obtain more O-compounds, mono-ring aromatics and aliphatics. Especially, the content of phenolics increases significantly from 15.49% to 35.17%, but the content of multi-ring aromatics decreases from 23.13% to 2.36%. By comparing the compositions of Py primary tar and G-K final tar, it is found that secondary reactions occurred during G-K pyrolysis process include the cleavage of alkane and esters, condensation of mono-ring aromatics with low carbon alkene, ring opening, isomerization of tri-ring aromatics, hydrogenation of aromatics and acids.

1. Introduction

Coal is a preferred energy source in China and will remain be a key role in China's energy sources [1]. Coal pyrolysis is the initial phase of coal conversion processes and has an important impact on the subsequent phases [2,3]. Usually, coal pyrolysis is classified according to the final temperature and the heating rate. Low temperature pyrolysis has many advantages, such as mild reaction conditions, simple process, low production cost, less investment and atmospheric pressure production, which can meet with the demand for energy saving and is deemed as an economical coal conversion process [4,5]. Slow pyrolysis is a relatively successful technology compared with fast pyrolysis [6]. But there are still many problems in slow pyrolysis, such as poor quality coal tar, only using lump coal, oil-dust separation difficulty, high cost of tar processing, pipeline blockage, and difficulty in wastewater treatment [7]. None of fast pyrolysis technologies were commercialized up to now. Therefore, understanding coal pyrolysis process and the difference between fast pyrolysis and slow pyrolysis are of great significance for coal conversion and utilization.

A lot of research has been done on coal pyrolysis and it has been found that many factors including coal rank, particle size, temperature, heating rate, atmosphere and reactor have significant effects on coal pyrolysis characteristics [8,9]. In slow pyrolysis process, coal macromolecular structure will gradually condense and become more stable. So for the same coal, as the heating rate increases, the coal conversion rate increases [10]. The presence of a purging gas can greatly avoid secondary reactions and is also dependent on the apparatus of choice [11]. Tian *et al.* [12] found that coke yields gradually increase with the decrease of heating rate by thermal gravimetric (TG) and Qiao *et al.* [13] reached the same conclusion. Liu *et al.* [14] pointed out that temperature increase is the smallest for volatiles generated in small fixed-bed reactors with a purging

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gas and extending residence time of volatiles at high temperature promotes conversion of tar to coke. Hayashi *et al.* [15] used Curie-point reactor and fixed-bed reactor to study fast and slow pyrolysis, respectively. He found that secondary reactions of volatiles are sufficiently suppressed in Curie-point reactor and the yield of pyrolysis gas remained unchanged or changed slightly with the increase of heating rate. Xu *et al.* [16] conducted pyrolysis tests in an improved fixed bed reactor and used Gray-King assay (G-K) as a comparison, found that the tar yield in the fixed bed reactor is higher than that of G-K. Liu *et al.* [17] pointed out that pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) is a powerful pyrolysis reactor without secondary reactions and the volatiles detected by Py-GC/MS are mainly generated by the cracking of related chemical bonds in coal molecular structure.

In this paper, the pyrolysis process of Shendong coal (SD) was first studied by combining the characteristics of TG, Py-GC/MS and G-K apparatus. The final pyrolysis temperatures of three pyrolysis reactors are all 600 °C. Two pyrolysis modes of Py-GC/MS, direct pyrolysis mode and collection trap mode, are adopted. Difference in the compositions of volatiles between Py direct fast pyrolysis and collection trap slow pyrolysis were compared. Then coke yields of different pyrolysis apparatus were analyzed and compared to quantitatively describe coal pyrolysis process. Finally, difference in the compositions between Py primary tar and G-K final tar were analyzed to illustrate the secondary reactions.

2. Experimental

2.1. Coal sample

Shendong coal (SD) was obtained from Shendong coal mine, located in Yulin city, Shaanxi province. SD coal was firstly crushed and then grounded to pass through an 80-mesh standard sieve (0.18 mm), subsequently dried at 105 °C in a vacuum for 4 h. Proximate and ultimate analyses were determined by Chinese national standard (GB/T 212—2008, GB/T 476—2001). Size distribution was measured according to international standard ISO13320-1. A summary of the proximate and ultimate analyses as well as the size distribution of SD coal were shown in Table 1.

2.2. TG experiment

TG has been widely used to study the characteristics of coal pyrolysis [18]. TG was performed on a TG-DTA/DSC analyzer (STA449F3, NETZSCH-Gerätebau GmbH, Germany). 15 mg SD coal was placed in a platinum crucible and heated from 40 °C to 600 °C at a heating rate of 5 °C·min^{-1}, and then held for 15 min. 50 ml·min^{-1} nitrogen was used as a purging gas. The heating procedure of TG is the same as that of G-K.

2.3. Py-GC/MS experiments

SD coal was pyrolyzed on a CDS 5200 pyrolyzer (CDS Analytical Inc., USA) coupled with a GC/MS (QP2010 plus, Shimadzu Inc., Japan) [19—21], which can provide two pyrolysis modes: direct pyrolysis mode and collection trap mode. During direct pyrolysis mode, the pyrolysis volatiles will be immediately transferred to GC/MS for detection by a purging gas. But during collection trap mode, the pyrolysis volatiles will be first collected in the cold trap at low temperature and then subjected to thermal desorption for GC/MS analysis, which allows the use of different reactive gases and the setting of pyrolysis temperature programs.

2.3.1. Direct pyrolysis mode

SD coal was directly pyrolyzed by Py-GC/MS at a heating rate of 1200000 °C·min^{-1} to the final pyrolysis temperature of 600 °C and held for 20 s, which was sufficient to complete the pyrolysis process [22]. The pyrolysis volatiles were transferred directly to GC/MS by 40 ml·min^{-1} helium. About 2 mg SD coal was placed at the center of the filament for pyrolysis and held in the place using two pieces of quartz wool. Before and after pyrolysis, one hundred thousand molecule-accurate weighing balance (ESJ80-5, China) was used to calculate the coke yield.

2.3.2. Collection trap mode

SD coal was also temperature programmed pyrolyzed by Py-GC/MS at a heating rate of 5 °C·min^{-1} to the final pyrolysis temperature of 600 °C and held for 15 min. The heating procedure was the same as that of G-K. The pyrolysis volatiles were first collected at −20 °C and then the cold trap was thermal desorption at 300 °C for 10 min and then was transferred to GC/MS by 40 ml·min^{-1} helium.

The detailed parameters of GC/MS have been reported in Ref. [23]. Fig. 1 is the schematic diagram of different modes of Py-GC/MS.

2.4. G-K experiment

G-K assay was carried out according to Chinese National Standard GB/T 1341—2007, which is a comprehensive test and pyrolysis products are divided into coke, liquid (tar and water) and gas [24]. G-K assay has the advantages of good gas tightness, less loss of pyrolysis products and usually used as a reference for industrial production [25]. Fig. 2 shows the schematic diagram of G-K pyrolysis apparatus. About 20 g SD coal was pyrolyzed at a heating rate of 5 °C·min^{-1} to the final pyrolysis temperature of 600 °C and held for 15 min without a purging gas. After pyrolysis, the liquid product was collected by an ice-water bath and total water content was determined by ASTM D95-2010. The yields of pyrolysis coke and liquid were obtained by weighing. The yields of pyrolysis gas, coal tar and pyrolysis water were obtained by Eqs. (1)–(3).

$$\mathrm{Yield_{gas}}=100\%-\mathrm{Yield_{coke}}-\mathrm{Yield_{liquid}} \quad (1)$$

$$\mathrm{Yield_{coal\ tar}}=\mathrm{Yield_{liquid}}-\mathrm{Yield_{total\ water}} \quad (2)$$

$$\mathrm{Yield_{pyrolysis\ water}}=\mathrm{Yield_{total\ water}}-\mathrm{M_{ad}} \quad (3)$$

Coal tar (without solvent dilution) was analyzed by Py-GC/MS at 300 °C that is consistent with the GC inlet temperature. The

Table 1
Conventional analyses and size distribution of SD coal

Proximate analysis (ad)/% (mass)				Ultimate analysis (daf)/% (mass)					Size distribution/μm			
M	A	V	FC	C	H	N	S	O*	D_{10}	D_{50}	D_{90}	RD
5.85	6.10	36.87	51.18	64.49	3.68	0.90	0.23	30.70	18.81	94.86	220.73	2.13

Note: daf—dry and ash-free basis, ad—air-dried basis, *By difference. D_{10}, D_{50}, D_{90}—10%, 50%, 90% of the particles are smaller than the diameter, respectively, RD=(D_{90}−D_{10})/D_{50}.

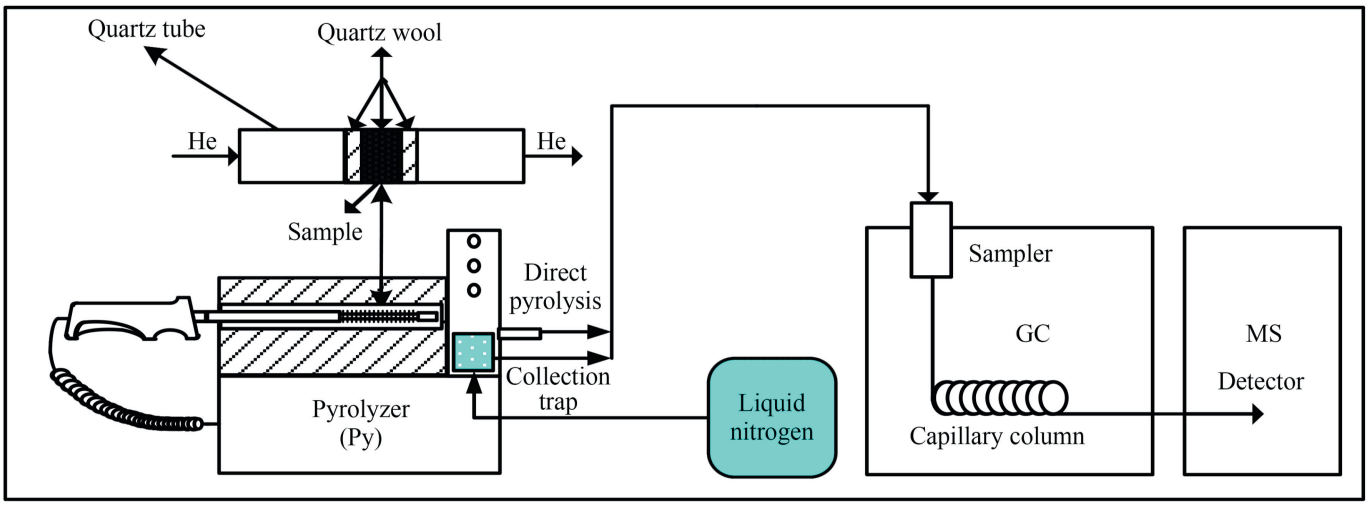

Fig. 1. Schematic diagram of different modes of Py-GC/MS.

composition of pure tar was obtained by using Py as an injector. The detailed tar separation process is as follows: The coal tar adhered to the inner wall of collection bottle, the quartz tube outlet, and the branch pipe were carefully washed by dichloromethane. The water in the washed coal tar was absorbed and removed by Na_2SO_4 and then Na_2SO_4 was removed by filtration with dichloromethane. Finally, dichloromethane was naturally dried [26].

3. Results and Discussion

3.1. TG analysis

TG and DTG curves of SD coal are shown in Fig. 3. Two obvious mass loss regions were found in DTG curve. The first mass loss of about 4% (mass) occurred in the temperature of <150 °C, accompanied by a DTG peak of about 70 °C, which was associated to the removal of physically absorbed moisture and gas from the atmosphere [27]. The second major mass loss occurred in 350–550 °C and is consider as the main volatiles release region [12]. The maximum mass loss temperature and maximum mass loss rate are 438.21 °C and 0.72%·min^{-1}, respectively. The coke yield was 73.11% (mass), which includes non-pyrolytic part of SD coal and the part caused by condensation reaction during slow pyrolysis process.

3.2. Py-GC/MS analysis

3.2.1. Direct fast pyrolysis

Coal pyrolysis, at heating rate of 1200000 °C·min^{-1} under 40 ml·min^{-1} helium, can be considered that there are no condensation and secondary reactions. Because coal was instantaneously pyrolyzed and pyrolysis volatiles was immediately removed from the high temperature zone. Therefore, the pyrolysis rate is highest and the coke yield is considered as non-pyrolytic part in coal. The pyrolysis rate and coke yield under direct fast pyrolysis mode of SD coal are 29.97% (mass) and 70.03% (mass), respectively.

The volatiles under direct fast pyrolysis will be discussed together with the volatiles under collection slow pyrolysis to illustrate the difference between fast pyrolysis and slow pyrolysis.

3.2.2. Collection slow pyrolysis

The total ion chromatograms and compositions of pyrolysis volatiles under direct fast pyrolysis and collection slow pyrolysis of SD coal were shown in Figs. 4 and 5. The corresponding chemical components of pyrolysis volatiles tested by GC/MS are shown in Table S1 and Table S2 in the Supplementary Material, respectively. All identified components were categorized as aliphatic hydrocarbon compounds (aliphatics), aromatic hydrocarbon compounds (aromatics), oxygen-containing compound (O-compounds) and

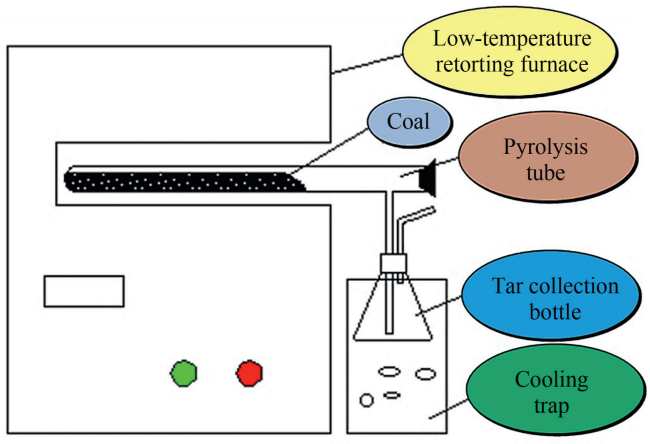

Fig. 2. Schematic diagram of G-K pyrolysis apparatus.

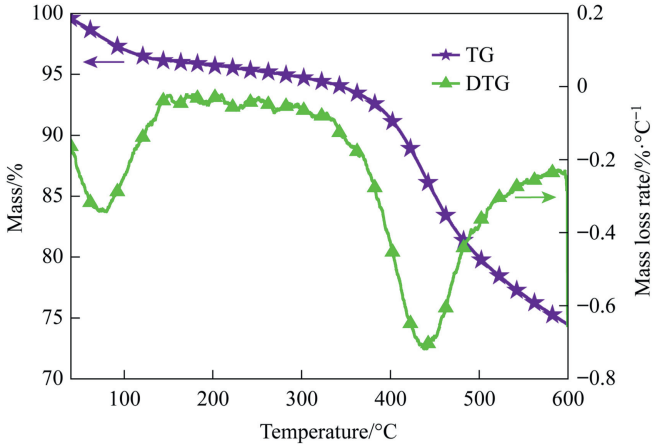

Fig. 3. TG and DTG curves of SD coal.

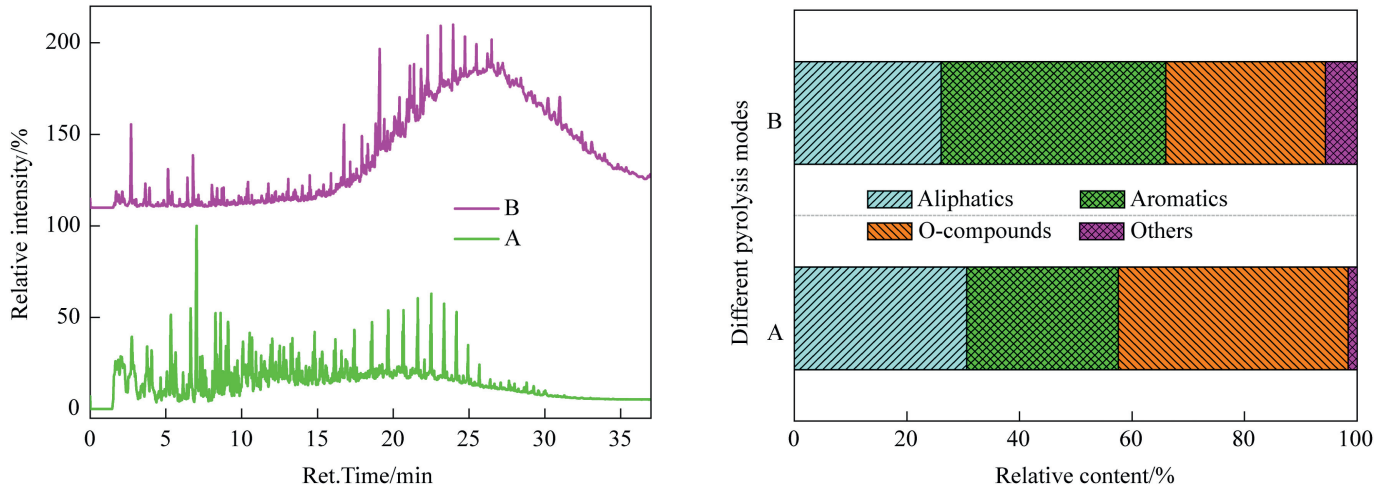

Fig. 4. Total ion chromatograms (left) and group composition (right) of the pyrolysis volatiles of SD coal under different pyrolysis modes of Py-GC/MS, A direct fast pyrolysis; B collection slow pyrolysis.

others. Aromatics were further subdivided into mono-ring, bicy-ring and multi-ring structures, O-compounds were further subdivided into phenolic compounds (phenolics), carboxylic acid compounds (carboxylic acids) and the remaining compounds.

Compared with slow pyrolysis, more O-compounds and aliphatics were obtained by fast pyrolysis and the content of O-compounds increased significantly from 28.39% to 40.81%, while aromatics content decreased from 39.93% to 26.93%. Although the change of the total amount of aliphatics was not obvious, the distribution of alkanes and alkenes changed significantly. In slow pyrolysis process, the majority of aliphatics (26.05%) was alkanes (21.47%), containing a small amount of alkenes (4.58%). Alkanes were mainly concentrated in C13—C21, the most significant alkenes is 2-methyl-2-butene. In fast pyrolysis process, 30.64% aliphatics include 19.55% alkane and 11.09% alkenes. Alkanes were mainly concentrated in C5—C21. Compared with slow pyrolysis, the content and carbon chains of alkanes decrease and the content of alkenes increases in fast pyrolysis, which indicates that fast pyrolysis has stronger fracture ability to coal molecules and alkenes might be hydrogenated to alkanes during slow pyrolysis.

Compared with slow pyrolysis, the total amount of aromatics obtained by fast pyrolysis decreased and the distribution of ring number was significantly different. More mono-ring and bicy-ring aromatics were obtained by fast pyrolysis and the content of mono-ring aromatics increased from 13.64% to 19.14%, the content of bicy-ring aromatics increased from 3.16% to 5.44%. While multi-ring aromatics content significantly decreased from 23.13% to 2.36%. Guo *et al.* [28] pointed out that the content of the mono-ring aromatics was closely related to heating rate and found that mono-ring aromatics content increased with the increase of heating rate, which is consistent with the results in this paper. Possible reasons are that multi-ring aromatics are further cleaved into mono-ring and bicy-ring aromatics during fast pyrolysis process, more multi-ring aromatics are formed due to condensation reaction during slow pyrolysis process. Compared with slow pyrolysis, the total amount of O-compounds obtained by fast pyrolysis increased. More phenolics were obtained by fast pyrolysis and the content of phenolics increased from 15.49% to 35.17%, while carboxylic acids content decreased from 5.03% to 0.67%. Tian *et al.* [12] found that phenols content gradually increased

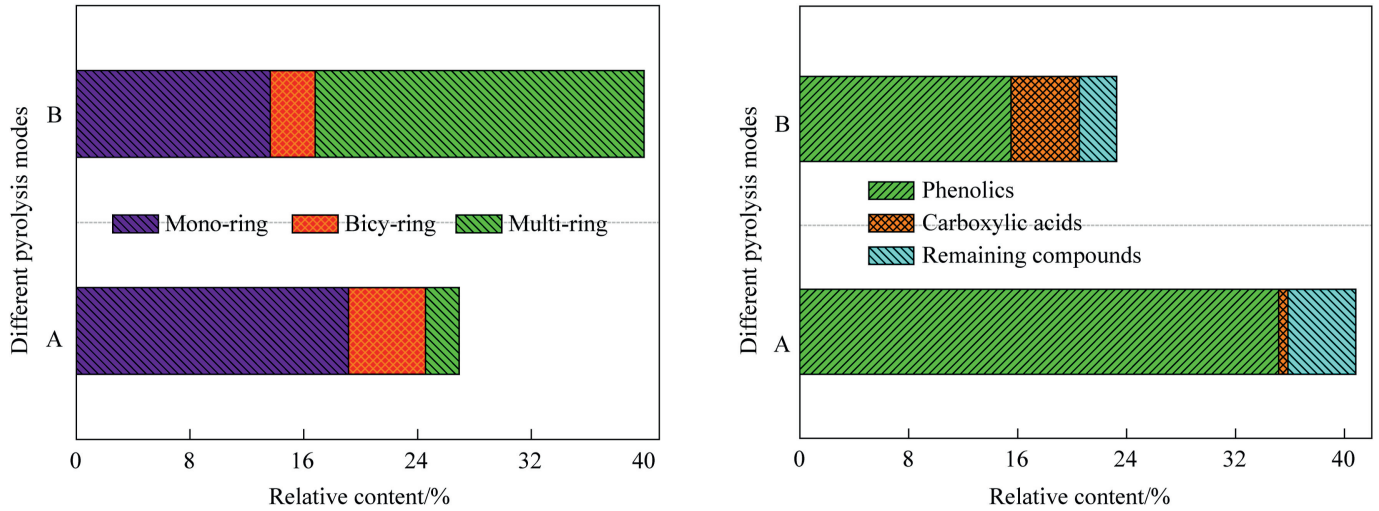

Fig. 5. Aromatics (left) and O-compounds (right) content of the pyrolysis volatiles of SD coal under different pyrolysis modes of Py-GC/MS, A direct fast pyrolysis; B collection slow pyrolysis.

with the increase of heating rate, which is consistent with the results in this paper.

3.3. G-K analysis

3.3.1. Yields of the G-K experiment

Table 2 shows the distribution of SD coal pyrolysis products. The coke yield of G-K was 76.35% (mass), which includes non-pyrolytic part of SD coal, the part caused by condensation reaction during slow pyrolysis process and the part caused by secondary reaction in the pyrolysis process without a purging gas. The liquid yield for SD coal during G-K pyrolysis process was 12.35% (mass), including 4.62% (mass) coal tar yield and 7.73% (mass) total water yield. The gas yield and pyrolysis water yield of SD coal during G-K pyrolysis process were 11.30% (mass) and 1.88% (mass), respectively.

3.3.2. Composition analysis of G-K tar and the secondary reactions

Secondary reactions during coal pyrolysis were still not well understood [29]. The primary volatiles [30] is assumed to undergo secondary reactions when it escapes from the central low-temperature coal layer [31]. It was difficult to obtain high yield of target products only by controlling the primary reaction alone, the secondary reactions should be understood and controlled as well [32]. In order to analyze secondary reactions during G-K assay process, the compositions of G-K final tar are discussed together with the results under Py collection trap mode. The heating procedure is the same for G-K and Py collection trap mode to ensure that the total pyrolysis volatiles in both are unchanged, the only difference is that Py has a purging gas, the generated pyrolytic volatiles will be removed from the high-temperature pyrolysis zone in time, which greatly avoids the occurrence of secondary reactions. So the compositions of pyrolysis volatiles under Py collection trap mode were regarded as the primary tar composition (without secondary reactions) of G-K final tar composition.

Fig. 6 shows the total ion chromatogram and composition of G-K final tar. The corresponding chemical components of G-K final tar tested by GC/MS are shown in Table S3 in the supplementary materials. Aliphatics were further subdivided into alkanes and alkenes, aromatics were further subdivided into mono-ring, bicy-ring, tri-ring, tetra-ring and >tetra-ring structures, O-compounds were further subdivided into alcohols, phenols, ethers, ketones, esters, aldehydes and acids, Other heteroatomic compounds were further subdivided into N-compounds, S-compounds and remaining compounds.

As can be seen from Fig. 6, compared with Py primary tar composition, G-K final tar composition changed significantly, mainly reflected in higher aliphatics content and lower aromatics content. There are more aliphatics in G-K final tar and the content increased significantly from 26.05% to 46.65%, while aromatics content decreased from 39.93% to 20.94%.

Fig. 7 shows the aliphatics and aromatics contents of Py primary tar and G-K final tar. In Py primary tar composition, 21.47% alkanes are mainly concentrated in C13—C21 and the most significant alkenes is 2-methyl-2-butene. In G-K final tar composition, 41.92% alkanes are mainly concentrated in C6—C32 and the low carbon alkene (2-methyl-2-butene) disappears. Compared with Py primary tar composition, alkanes content in G-K final tar increases and carbon chain number distribution of alkanes becomes wider, which might be caused by alkane cracking (C21—C6+C15) during G-K pyrolysis process [33]. Compared with Py primary tar composition, the distribution of aromatic ring number in G-K final tar changed significantly. The contents of mono-ring, tetra-ring and >tetra-ring aromatics decreased obviously, while the contents of bicy-ring and tri-ring aromatics in G-K final tar increased. Especially, the mono-ring content decreased from 13.64% to 4.09% and >tetra-ring aromatics disappeared in G-K final tar.

The disappearance of low carbon alkene and the significant reduction of the mono-ring aromatics content in G-K final tar may be attributed to the secondary reactions of low carbon alkene and mono-ring aromatics to form bicy-ring aromatics. The disappearance of methylindene in G-K final tar may be attributed to ring opening or aromatization reaction. In Py primary tar, only anthracene and its derivatives were found but no phenanthrene and its derivatives. While anthracene, phenanthrene and their derivatives were found in G-K final tar, which indicates that the isomerization of tri-ring aromatics occurred during G-K pyrolysis process. Compared with Py primary tar composition, partial hydrogenation saturated rings of tetra-ring aromatics were found in G-K final tar, which indicates that hydrogenation reaction occurred during G-K pyrolysis process. The disappearance of >tetra-ring aromatics in G-K final tar is attributed to their residue in G-K coke.

Table 2
Distribution of SD coal pyrolysis products

	Coke	Gas	Liquid	Tar	Total water	Pyrolysis water
Yield/% (mass)	76.35	11.30	12.35	4.62	7.73	1.88

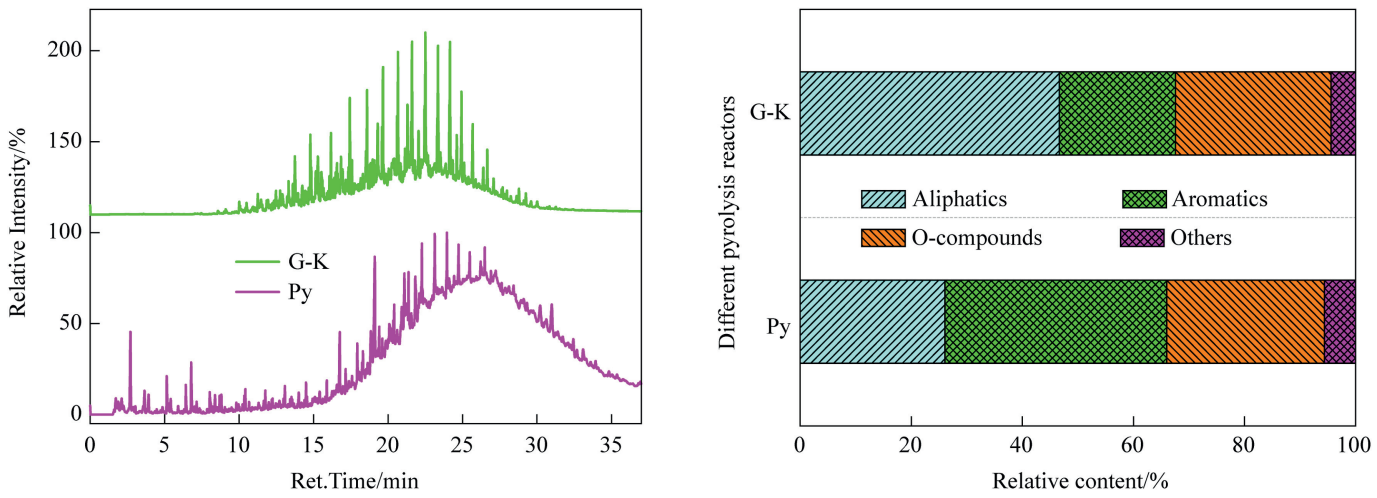

Fig. 6. Total ion chromatograms (left) and group compositions (right) of Py primary tar and G-K final tar.

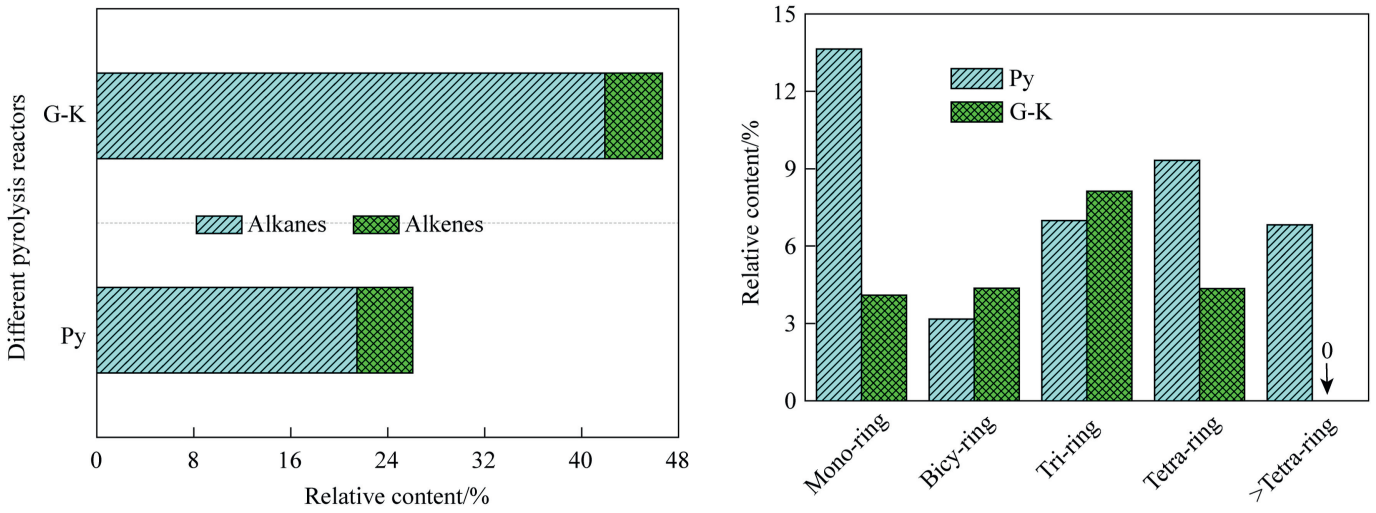

Fig. 7. Aliphatics (left) and aromatics (right) contents of Py primary tar and G-K final tar.

Fig. 8 shows the O-compounds and other heteroatomic compounds content of Py primary tar and G-K final tar. Compared with Py primary tar composition, the total amount of O-compounds in G-K final tar did not change significantly, while the composition distribution of O-compounds was significantly different. Compared with Py primary tar composition, the contents of alcohols, ethers, and aldehydes in G-K final tar increased, and the contents of ketones, esters, and acids decreased. Clearly, alcohols content in G-K final tar increased from 0.64% to 3.28% and aldehydes content increased from 0% to 0.14%, while acids content decreased from 10.09% to 5.03% and esters content decreased from 1.25% to 0.23%, which are attributed to the hydrogenation of acids to produce aldehydes and alcohols and the cleavage of esters to produce acids, aldehydes or alcohols. Other heteroatomic compounds are mainly N-compounds. Compared with Py primary tar composition, the species of nitrogen and sulfur compounds are more diverse in G-K final tar and similar findings were observed by Leblanc *et al.* [34]. Meanwhile, Xu *et al.* [35] found that secondary reactions will increase heteroatomic compounds content, which was consistent with the result in this paper that the content of S-compounds in G-K final tar increased from 0% to 0.40%. In brief, the secondary reactions during G-K assay process can be summarized as the cleavage of alkane and esters, condensation of mono-ring aromatics with low carbon alkene, ring opening, isomerization of tri-ring aromatics, hydrogenation of aromatics and acids [36].

3.4. Quantitative analysis of SD coal pyrolysis process

Table 3 shows the characteristics of different pyrolysis reactors and their coke yield. The final pyrolysis temperatures of three pyrolysis reactors are all 600 °C, the difference is the heating rate and the presence or absence of a purging gas. G-K fixed bed will make pyrolysis volatiles experience a higher surrounding temperature and the secondary reactions were inevitable. Py can realize instantaneous pyrolysis and pyrolysis volatiles will be immediately removed from the high temperature zone, which can greatly avoid condensation reaction during slow pyrolysis process and greatly avoid secondary reactions due to the absence of a purging gas. As

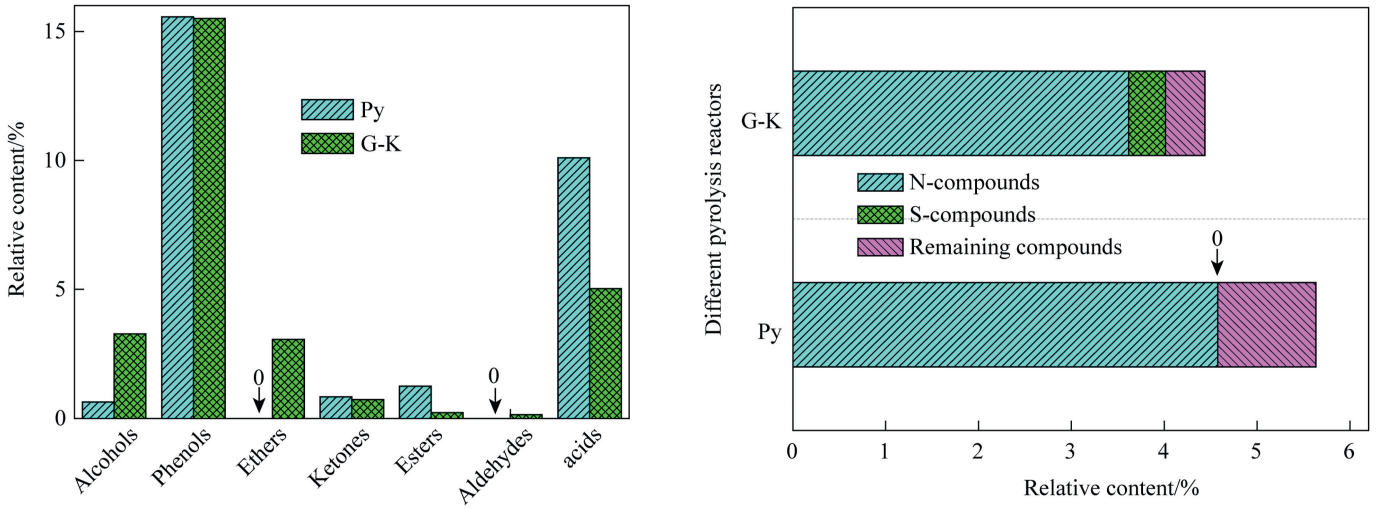

Fig. 8. O-compounds (left) and other heteroatomic compounds (right) content of Py primary tar and G-K final tar.

Table 3
Characteristics of different pyrolysis reactors and their coke yields

Reactors	G-K	TG	Py
Heating rate/°C·min^{-1}	5	5	1200000
End temperature/°C	600	600	600
Purging gas	No	Yes	Yes
Condensation reaction	Yes	Yes	No
Secondary reaction	Yes	No	No
Coke yield/% (mass)	76.35	73.11	70.03

Table 4
Quantitative calculation results of SD coal pyrolysis process

	Yield/% (mass)
G-K coke (X_1)	76.35
TG coke (X_2)	73.11
Py coke (X_3)	70.03
Py volatiles ($X_4 = 100–X_3$)	29.97
Source of coke (X_1)	
Condensation reaction ($X_5 = X_2–X_3$)	3.08
Non-pyrolytic part (X_3)	70.03
Secondary reaction ($X_6 = X_1–X_2$)	3.24
G-K gas and total water (X_7)	19.03
G-K tar (X_8)	4.62
Primary tar ($X_9 = X_4–X_7$)	10.94
Primary tar consumption (X_9)	
Secondary reaction (X_6)	3.24
Final tar (X_8)	4.62
Loss part (X_{10})	3.08

can be seen from Table 3, the order of the coke yield is G-K>TG>Py. The difference between TG and Py is that the heating rate of TG is slow and condensation reaction occurs in TG pyrolysis process, so the yield of TG coke is higher than that of Py coke and the higher part is attributed to condensation reaction during slow pyrolysis process. The difference between G-K and TG is that there is no purging gas in G-K pyrolysis process, so the yield of G-K coke is higher than that of TG coke and the higher part is attributed to secondary reaction during G-K pyrolysis process. Therefore, there are three sources of G-K coke, including non-pyrolytic part of SD coal, the part caused by condensation reaction and the part caused by secondary reaction.

Table 4 shows the quantitative calculation results of SD coal pyrolysis process. The minimum Py coke yield is considered to be non-pyrolytic part of SD coal. The yield of TG coke (73.11% (mass)) is higher than that of Py coke (70.03% (mass)) and the higher part (3.08% (mass)) is caused by condensation reaction during slow pyrolysis process. The yield of G-K coke (76.35% (mass)) is higher than that of TG coke (73.11% (mass)) and the higher part (3.24% (mass)) is caused by secondary reaction during G-K pyrolysis process. As can be seen from Table 4, the non-pyrolytic part (Py coke yield) of SD coal is 70.03% (mass) and the maximum pyrolysis volatiles is 29.97% (mass). G-K coke yield caused by condensation reaction and secondary reaction accounts for 3.08% (mass) and 3.24% (mass), respectively. Primary tar of SD coal is 10.94% (mass), of which the generated final tar is 4.62% (mass), the secondary reaction consumption is 3.24% (mass) and the loss part due to cooling escape is 3.08% (mass).

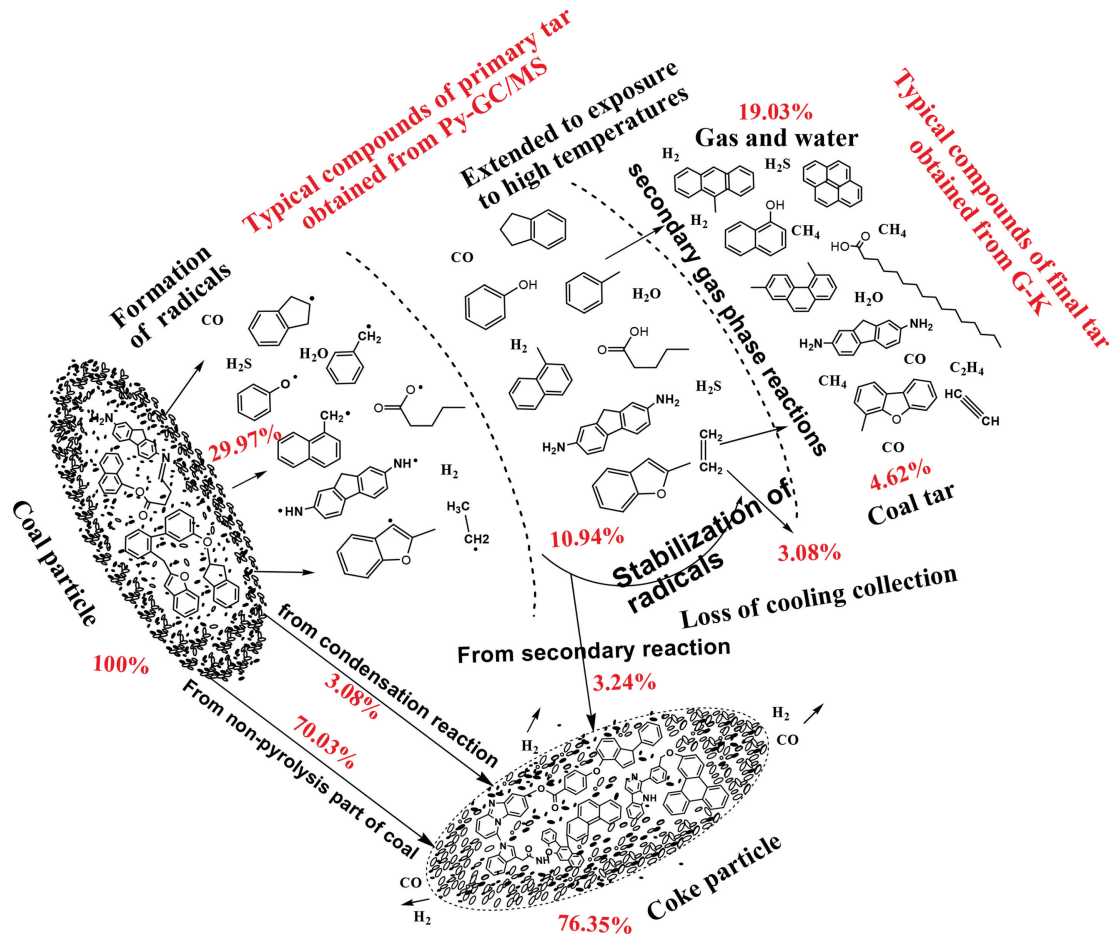

Fig. 9. Schematic diagram of SD coal quantitative pyrolysis process.

It is well accepted that coal pyrolysis follows a radical mechanism proposed by Tromp [37]. Liu [38] modified the coal pyrolysis reaction mechanism and pointed out that coal cannot be completely volatilized and coke can be directly generated from the nonvolatile part in coal, not just from polymerization and condensation reactions of the volatiles. Then on the basis of the pyrolysis mechanism proposed by Tromp and Liu, Sun *et al.* [39] further proposed the swelling coal in-situ catalytic pyrolysis mechanism. Fig. 9 shows the schematic diagram of SD coal quantitative pyrolysis process. In Fig. 9, black spots in coal and coke particles denote the nonvolatile parts. The radicals generated by coal pyrolysis have extremely short existence time and strong reactivity, which is difficult to track their reaction pathways [40]. Radicals are usually analyzed and speculated by indirect method. The typical compounds in Py primary tar and G-K final tar are also shown in Fig. 9.

4. Conclusions

The method in this paper attempts to quantitatively analyze the condensation reaction and secondary reaction during coal pyrolysis, and explain the secondary reactions to a certain extent. (1) There are three sources of G-K coke (76.35% (mass)), including nonpyrolytic part of SD coal (70.03% (mass)), the part caused by condensation reaction (3.08% (mass)) and the part caused by secondary reaction (3.24% (mass)). (2) Alkanes were mainly concentrated in C13−C21 and C5−C21 in slow and fast pyrolysis process, respectively. Compared with slow pyrolysis, alkenes content obtained by fast pyrolysis increased from 4.58% to 11.09%. More mono-ring aromatics were obtained by fast pyrolysis and the content of mono-ring aromatics increased from 13.64% to 19.14%, while multi-ring aromatics content significantly decreased from 23.13% to 2.36%. More phenolics were obtained by fast pyrolysis and the content of phenolics increased from 15.49% to 35.17%, while carboxylic acids content decreased from 5.03% to 0.67%. (3) Compared with Py primary tar composition, there are more aliphatics in G-K final tar and the content increased significantly from 26.05% to 46.65%, while aromatics content decreased from 39.93% to 20.94%. Total amount of O-compounds in G-K final tar did not change significantly, while the composition distribution of O-compounds was significantly different. The species of nitrogen and sulfur compounds are more diverse in G-K final tar.

CRediT Authorship Contribution Statement

Xiaoping Su: Writing – original draft, Formal analysis. Zhao Wang: Conceptualization. Ning Li: Data curation. Longjian Li: Software. Ping Zhang: Funding acquisition. Ming Sun: Writing – review & editing, Methodology. Xiaoxun Ma: Methodology, Funding acquisition.

Declaration of Competing Interest

All authors disclosed no relevant relationships.

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Supplementary Material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cjche.2024.08.004.

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