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Pyrolysis Behavior of Weakly Reductive Coals from Northwest China

Yunpeng Zhao, Haoquan Hu,* Lijun Jin, Bo Wu, and Shengwei Zhu

Institute of Coal Chemical Engineering, School of Chemical Engineering, Dalian University of Technology, 129 Street, Dalian 116012, People's Republic of China

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Pyrolysis behaviors of three weakly reductive coals from northwest China and one reductive Pingshuo (PS) coal were investigated in a thermogravimetric analyzer and a fixed-bed reactor. The results show that the pyrolysis behaviors of the weakly reductive coals are obviously different from that of the reductive coal despite their similar elemental composition. Compared with PS coal, the weakly reductive coals exhibit a lower weight loss and a lower rate of weight loss, and the peaks corresponding to the maximum rate of weight loss shift to high temperature. During pyrolysis in a fixed-bed reactor, the conversion and tar and gas yields of all the coals increase with temperature. The weakly reductive coals have lower conversions and tar yields than PS coal in the temperature range investigated, which is accordant with the weight loss in thermogravimetric analysis. The tars from coal pyrolysis were characterized by FT-IR, ultimate analysis, and ^{1}H NMR, and the combustion behavior of chars from different coals was compared on a thermogravimetric analyzer.

1. Introduction

Abundant Jurassic coalfields, such as Shendong coal in Shanxi, Lingwu coal in Ningxia, and Hami coal in Xinjiang province, exist in the northwest of China and play an important role in China's energy supply. These Jurassic coals were formed in an inland gathering environment. Most of the coal seams formed in a peat bog which was covered with shallow water, frequently exposed to air, and subjected to strong oxidative but weakly reductive effects during the accumulation process; therefore, they have weak gelatification but strong fusinization. Named after the process of coalification, these weakly reductive coals have characteristics of typically weak reducibility, such as low ash, sulfur, and phosphorus contents but high calorific value and aromatic structure.

Coal pyrolysis is one of the most important aspects of coal behavior because it occurs in all major coal utilization processes, such as combustion, gasification, carbonization, and liquefaction, etc. Therefore, understanding pyrolysis behavior is important to develop new coal utilization technologies and provide information about the composition and physicochemical structure of coal.[1−4] Many research works on coal pyrolysis were conducted by using a thermogravimetric analyzer, a fixed-bed reactor, or other reactors in the past.[5−10] Additionally, some modern characteristic methods have also been applied to analyze coal and the products from pyrolysis for identifying more detailed structure information and potential utilization.[11−15] Previous work indicated that the weakly reductive coals present physicochemical properties different from those of common coals,[16] but little information about their thermal behavior was reported. To rationally utilize these weakly reductive coals, it is essential to know the pyrolysis behavior and characteristics of the products formed during pyrolysis.

Thermogravimetric analysis (TGA) is a useful technique to obtain the weight loss and rate of weight loss of coals with

* To whom correspondence should be addressed. Telephone and fax: +86-411-39893966. E-mail: hhu@chem.dlut.edu.cn.

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Table 1. Analyses of Coal Samples

	proximate analysis (wt %)			ultimate analysis (wt % daf)					petrographic analysis (vol %)			
coal sample	M_{ad}	A_d	V_{daf}	C	H	N	O^a	S	vitrinite	inertinite	exinite	calorific value (kJ/g daf)
PS	2.23	17.93	37.19	80.41	5.20	1.38	11.95	1.06	47.5	44.8	7.7	32.5
SD	9.80	4.50	33.72	79.53	4.16	0.91	14.93	0.48	41.2	58.4	0.4	30.1
LW	12.60	5.16	30.91	79.71	3.84	0.71	15.29	0.45	22.8	75.3	0.8	30.0
HM	7.51	4.67	24.52	83.26	3.44	0.77	12.20	0.33	2.7	91.9	2.4	31.9

[a] By difference.

Table 2. Ash Composition of Coal Samples (wt % db)

coal sample	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	SO_3	K_2O	Na_2O	P_2O_5
PS	48.31	44.66	2.25	1.97	1.33	0.13	0.21	0.17	0.06	0.51
SD	23.28	9.66	15.98	0.84	27.48	3.23	14.23	0.08	2.30	0.03
LW	13.14	5.59	22.15	0.42	25.80	14.42	13.72	0.28	3.90	0.05
HM	13.30	10.55	27.38	0.44	32.52	1.96	8.78	0.07	1.10	0.75

increasing temperature, which can be used to determine the pyrolysis reactivity and mechanism of coals. In a fixed-bed reactor, the pyrolysis products can be collected during coal pyrolysis for further analysis using all kinds of modern characterization techniques. The results from both TGA and the fixed-bed reactor will be helpful to understand the structure characteristics and composition information of coals and their pyrolysis products. On the basis of these results, chemical engineers can choose appropriate utilization technologies or develop new coal utilization technologies, such as the coal pyrolysis based cogeneration process or coal decoupling thermochemical conversion.

This work was aimed to investigate the pyrolysis behavior and the product distribution of weakly reductive coals in a thermogravimetric analyzer and a fixed-bed reactor. Pingshuo coal, a typical reductive coal in China, was used for comparison. The tar and char obtained from coal pyrolysis were analyzed using FT-IR, ultimate analysis, ^1H NMR, and TGA.

2. Experimental Section

2.1. Coal Samples. Three weakly reductive coal samples, Shendong coal (SD), Lingwu coal (LW), and Hami coal (HM), and a reductive coal sample, Pingshuo coal (PS), for comparison were investigated. All coal samples studied were ground to below 100 mesh. The chemical and petrographic analysis results of these coal samples are shown in Table 1, and their ash compositions are listed in Table 2. From Table 1, four coal samples have very similar carbon content, while the weakly reductive coal samples show low ash and high inertinite contents. From Table 2, the ash composition of PS coal mainly contains SiO_2 and Al_2O_3, while the weakly reductive coals have high CaO and Fe_2O_3 contents.

2.2. Thermogravimetric Analysis. TG analysis was performed on a Mettler Toledo TGA/SDTA851^e analyzer. During the experiment, about 15 mg of the coal sample was placed in a ceramic crucible and heated from 25 to 900 °C with a heating rate of 10 °C/min using N_2 as the carrier gas at a constant flow rate of 60 mL/min.

2.3. Pyrolysis in a Fixed-Bed Reactor. Coal pyrolysis was carried out in a vertical fixed-bed reactor. The apparatus and process have been described in the literature.[17,18] Briefly, approximately 5 g of the coal sample was placed in the center of the reactor. The furnace was first heated to the desired temperature, and then the reactor was loaded in the center of the furnace. The heating time from ambient temperature to reaction temperature (from 400 to 650 °C) was about 10 min, and the sample was held at the reaction temperature for 30 min. The volatile matter during coal pyrolysis was brought out by high-purity nitrogen as the carrier from the reactor to the cool trap. The liquid products (tar plus water) were cooled by a cool trap below the reactor, and the gases were collected by a gas bag for analysis. The solid char was removed from the reactor after the experiment and weighed, and the gas yield was calculated by difference. The tar and water were separated by the method of ASTM D95-05^{e1} (2005). In the calculation of the conversion and yields, all were expressed on a dry-ash-free (daf) basis.

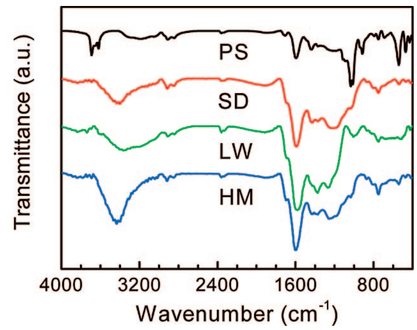

Figure 1. FT-IR spectra of coal samples.

2.4. Characterization. The products obtained from coal pyrolysis at 650 °C were analyzed. The elemental composition of tar and char was determined on a Vario EL III instrument. The FT-IR spectra of the raw coal and tar were measured by an EQUINOX55 spectrometer using KBr pellet technique. The ratio of coal or tar to KBr is about 1:160. The spectra were recorded from 4000 to 400 cm^{-1} at 2 cm^{-1} resolution. ^1H NMR of the tars was obtained at a H frequency of 400 MHz using a Varian INOVA 400 instrument. The combustion behavior of the char was conducted under an air flow of 60 mL/min at a heating rate of 10 °C/min from 25 to 800 °C in the TGA/SDTA851^e analyzer by temperature-programmed combustion (TPC). The compositions of gas products were analyzed by 5A molecular sieves and GDX502 columns using a 7890T gas chromatograph with a thermal conductive detector.

3. Results and Discussion

3.1. FT-IR Analysis. Figure 1 shows the FT-IR spectra of four coal samples. Compared with the reductive PS coal, these three weakly reductive coals have strong intensities of peaks attributed to −OH (3660−3200 cm^{-1}) and aromatic C=C (1650−1550 cm^{-1}). Due to the higher ash content, the FT-IR spectrum of PS coal shows obviously stronger peaks attributed to kaolinite (3690 cm^{-1}) and silicates (1090−840 cm^{-1}).

3.2. Thermogravimetric/Differential Thermogravimetric (TG/DTG) Analysis. The TG/DTG curves of coal samples are shown in Figure 2. Compared with those of PS coal, the weight loss and rate of weight loss of the weakly reductive coals are lower and the peaks of DTG shift to higher temperature, which can be ascribed to more inertinite content and the stable structure of the weakly reductive coals compared to those of PS coal. In addition, there exist small peaks in the DTG curves of weakly reductive coals, which are mainly attributed to the thermal decomposition of carbonate in coal at

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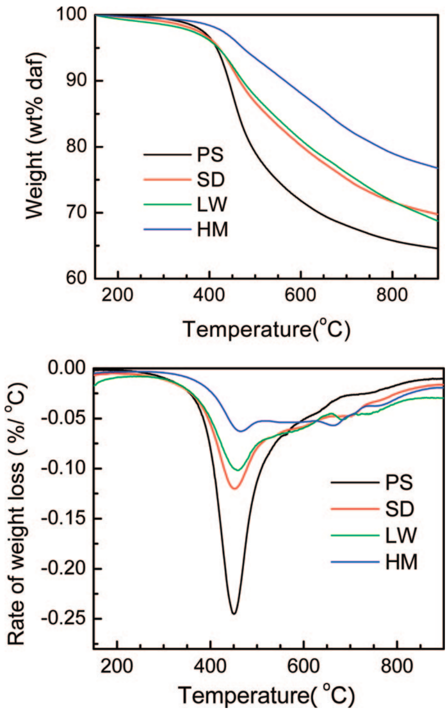

Figure 2. TG/DTG curves of coal samples.

Table 3. Characteristic Parameters on TG/DTG Curves of Coal Samples

coal sample	$W_{150-900°C}$ (wt %)	$W_{150-350°C}$ (wt %)	$W_{350-550°C}$ (wt %)	$W_{550-900°C}$ (wt %)	T_{max}
PS	34.7	1.6	21.5	11.6	451
SD	30.2	1.8	16.6	12.5	450
LW	31.2	2.2	13.6	15.4	458
HM	23.2	0.9	9.2	13.1	465

high temperature according to our previous studies on their pyrolysis behaviors by online TG/MS. [19]

The significant parameters obtained from the TG/DTG curves, such as the total weight loss ($W_{150-900°C}$), the weight loss at different temperature intervals, and the temperature corresponding to the maximum weight loss rate (T_{max}) are given in Table 3. For all the coals studied, the weight loss between 150 and 350 °C, mainly from distillation of the mobile phase and the thermal decomposition of weak bonds, is small. Weight loss mainly takes place in the temperature range between 350 and 550 °C, due to the degradation of the carbonaceous matrix and the evolution of relatively high molecular weight species, and decreases with an increase of the inertinite content in coal. The proportion of weight loss between 550 and 900 °C, which is ascribed to the condensation of the aromatic ring and the decomposition of mineral matter, increases with the inertinite content in coal.

3.3. Product Distribution. To examine the effect of temperature on the pyrolysis performance of the weakly reductive coals in the fixed-bed reactor, experiments were carried out at the main pyrolysis temperature range from 400 to 650 °C, on the basis of the TG/DTG curves. Figure 3 shows the pyrolysis product distribution at the temperature investigated. Clearly, the char yield decreases with an increase of the final pyrolysis temperature for all coal samples, which results from deeper decomposition of coal at higher temperature. Compared with the reductive PS coal, the weakly reductive coals have a higher char yield, and the yield increases with an increase of the inertinite content in coal.

The tar yield of all samples increases with temperature; however, the effect of temperature on the tar yield of PS coal is more obvious than that of the weakly reductive coals. At 650 °C, the tar yield of PS coal is 17.9%, about half the total volatile matter, but only 12.0%, 7.6%, and 6.7% for SD, LW, and HM coals, respectively, were obtained, which are obviously lower than half their total volatile matter. The change can be ascribed to the lower volatile matter, higher inertinite content, and also more volatile matter decomposing to gas products of the weakly reductive coals.

The gas yield of the weakly reductive coals rapidly increases with temperature, especially for LW and HM coals, but little change occurs at temperatures above 500 °C for PS coal. At high pyrolysis temperature, the gas yield of the weakly reductive coals is higher than that of PS coal. During coal pyrolysis, the formation of water is generally attributed to the esterification and dehydration reaction of the phenolic hydroxyl and carboxyl groups in coal.[20] The water yield of all coals increases with temperature. PS coal has a higher water yield than the weakly reductive coals at high pyrolysis temperature.

3.4. Product Analysis. The elemental compositions of tar from different coal pyrolyses are given in Table 4. It can be seen that the tars obtained from the weakly reductive coals have an elemental composition similar to that of the tar obtained from the reductive PS coal. Comparing the data in Tables 1 and 4, tar has a lower oxygen but a higher nitrogen content than the coal sample. The low oxygen content of tar is beneficial for its further process.[21] However, the higher nitrogen content is a disadvantage for its utilization.

The functional groups of tars were analyzed by FT-IR, and the results are shown in Figure 4. Compared with the coal sample, tar has strong intensities of peaks attributed to the aliphatic C−H vibration (3000−2800, 1350, and 1475 cm^{-1}), aromatic ring C−H vibration (3100−3000 cm^{-1}), C═O vibration (1750−1650 cm^{-1}), and substituents in the aromatic ring vibration (900−700 cm^{-1}). Moreover, the tars obtained from the weakly reductive coals, especially that from HM coal, have stronger intensities of peaks attributed to O−H (3400−3200 cm^{-1}), C−O−C (1275−1070 cm^{-1}), C═C (1675−1575 cm^{-1}), and substituents in the aromatic ring (900−700 cm^{-1}) than those of the tar from reductive PS coal, indicating that the tars from the weakly reductive coals have more oxygen-containing and aromatic compounds than that from PS coal.

The hydrogen distributions in tars obtained by ^{1}H NMR analysis are given in Table 5. The results show that the tars from the weakly reductive coals contain more aliphatic hydrogen at carbon atoms bonded to other aliphatic carbon atoms but lower aliphatic hydrogen adjacent to aromatic alkene groups than that from PS coal. In addition, the tar from HM coal contains a higher concentration of aromatic compounds than that from other coals, which may be ascribed to the highest inertinite content in HM coal.

Table 6 shows the proximate and ultimate analyses of pyrolysis chars. It is clear that the chars from the weakly reductive coals have slightly higher volatile matter and much lower ash content than that from the reductive PS coal. The

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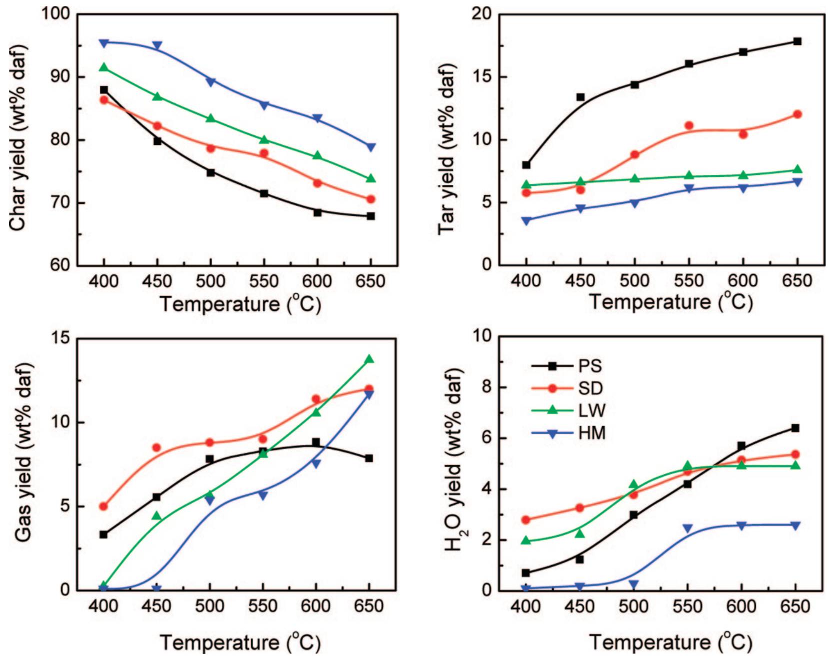

Figure 3. Effect of the pyrolysis temperature on product yields.

Table 4. Elemental Composition of Tars from Coal Pyrolysis in a Fixed-Bed Reactor

	ultimate analysis (wt % daf)				
coal sample	C	H	N	S + O[a]	H/C molar ratio
PS-tar	83.61	7.77	3.08	5.54	1.12
SD-tar	84.37	8.10	2.51	5.02	1.15
LW-tar	80.58	8.35	3.76	7.31	1.24
HM-tar	85.25	7.30	2.43	5.02	1.03

[a] By difference.

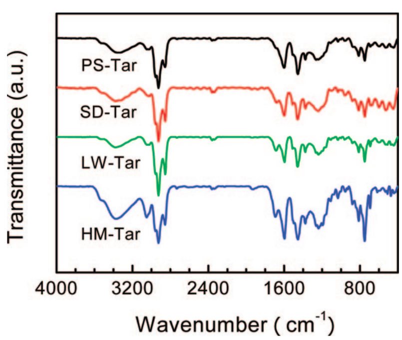

Figure 4. FT-IR spectra of tars.

Table 5. ^{1}H NMR Results of Tars from Coal Pyrolysis in a Fixed-Bed Reactor at 650 °C

		H content (mol %)			
hydrogen type	δ (ppm)	PS-tar	SD-tar	LW-tar	HM-tar
aromatic	6.3−9.3	32.11	32.68	31.31	41.36
alkene	4.5−6.3	4.46	2.94	5.73	1.10
aliphatic adjacent to oxygen	3.3−4.5	1.20	1.63	2.19	1.17
aliphatic adjacent to aromatic alkene group	1.8−3.3	30.21	21.90	23.11	22.89
other aliphatic (bonded to aliphatic only)	0.4−1.8	32.02	40.85	37.66	32.93

results may be explained from the TG/DTG data and analyses of coal samples. TG/DTG data in Figure 2 showed that the reductive PS coal has higher weight loss, indicating that the volatile matter of the reductive coal is more easily decomposed to gases and tar than that of the weakly reductive coals during pyrolysis. The proximate analysis of coal samples in Table 1 showed that the weakly reductive coals have obviously lower

Table 6. Analyses of Chars from Coal Pyrolysis in a Fixed-Bed Reactor at 650 °C

	proximate analysis (wt %)			ultimate analysis (wt % daf)					calorific value
sample	M_{ad}	A_d	V_{daf}	C	H	N	O[a]	S	(kJ/g daf)
PS-char	3.33	23.17	8.64	89.50	2.61	1.78	5.66	0.45	32.8
SD-char	4.52	5.93	9.76	92.20	2.81	1.19	3.44	0.36	33.0
LW-char	2.25	5.91	10.10	89.20	2.62	0.95	6.94	0.29	34.1
HM-char	2.56	5.76	10.66	90.32	2.59	0.81	6.09	0.19	34.3

[a] By difference.

ash content than the reductive PS coal, and the ashes of the weakly reductive coals in Table 2 contain a high CaO content, which may be as carbonate in coal and can decompose during pyrolysis. In addition, oxygen-containing and sulfur-containing functional groups and pyrite in coal are relatively easy to decompose to gases during pyrolysis, and the fixation of free radical fractions needs to consume hydrogen from condensation of aromatic and hydroaromatic structures at high temperature, so the char contains high carbon and nitrogen contents but low hydrogen, oxygen, and sulfur contents compared with raw coal.

The combustion TG/DTG profiles of chars are shown in Figure 5. The "ignition temperature", "peak temperature", and "burning out temperature" are the important characteristic temperatures on the combustion profile.[22,23] The ignition temperature is defined to be the point where the burning profile undergoes a sudden rise. The peak temperature is that on the burning profile where the weight loss rate is maximum. The burning out temperature is that where the sample oxidation is completed. The weight loss rate at peak temperature is named the "maximum combustion rate". A lower peak temperature means more reactivity of the char.[24,25] The characteristic

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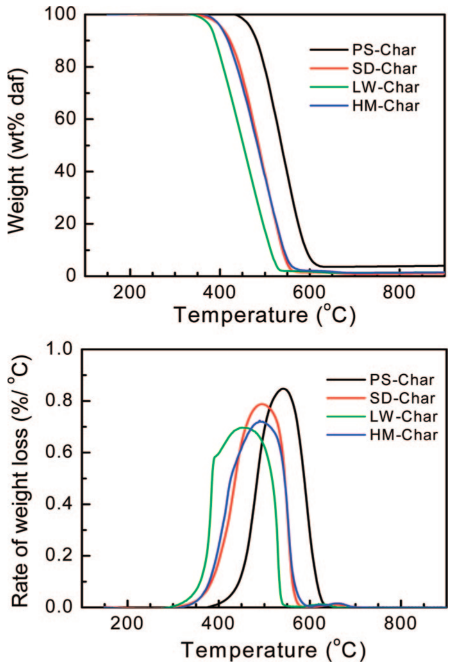

Figure 5. TG/DTG curves of char combustion.

Table 7. Characteristic Temperatures and Maximum Combustion Rate of Chars from TG/DTG Curves

sample	ignition temp (°C)	peak temp (°C)	burning out temp (°C)	max combustion rate (%/°C)
PS-char	395	543	632	0.847
SD-char	329	495	576	0.788
LW-char	310	451	541	0.697
HM-char	337	490	590	0.724

temperatures and maximum combustion rate of all chars are given in Table 7. It can be seen that the TG/DTG profiles of the chars from weakly reductive coals locate in the lower temperature region and all the characteristic temperatures are lower than those of char from PS coal, suggesting that the chars of the weakly reductive coals are more reactive and more easily burned than that of PS coal. Some researchers found that an alkali metal had a catalytic effect on the char combustion reaction.[26−28] Therefore, higher combustion reactivity of the chars from the weakly reductive coals may be partly caused by more alkali metal, which can be seen from the analysis of the ash composition in Table 2. In addition, the higher ash content and thermoplasticity of the PS-char can block off mass and heat transfer during combustion of the organic matrix.

To examine the combustion performance, the kinetics of char combustion was analyzed. The kinetic parameters, activation energy, and pre-exponential factor of char combustion were determined by assuming a first-order reaction using an integral method. The detailed depiction can be found in another paper.[18] The char combustion reaction equation can be simply expressed as the following formula:

$$-\frac{dx}{dt} = k(1-x) = A\exp\left(-\frac{E}{RT}\right)(1-x) \tag{1}$$

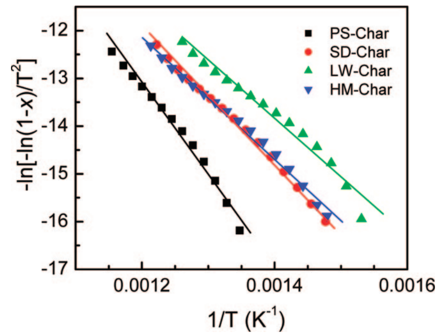

Figure 6. $-\ln[-\ln(1 - x)/T^2]$ vs $1/T$ for char combustion.

Table 8. Kinetic Parameters of Char Combustion

sample	temp range (°C)	activation energy E (kJ/mol)	pre-exponential factor A (min^{-1})	R^{2a}
PS-char	469−594	154.1	8.06×10^5	0.984
SD-char	404−545	116.7	6.20×10^3	0.996
LW-char	380−520	100.3	6.27×10^2	0.970
HM-char	403−551	107.4	1.01×10^3	0.988

[a] R = correlation coefficient.

Table 9. Compositions of Gas from Coal Pyrolysis in a Fixed-Bed Reactor at 650 °C

coal sample	gas yield (wt % daf)	gas composition (vol %)					
		H_2	CH_4	CO	CO_2	C_2H_6	C_2H_4
PS	7.87	44.82	38.49	9.89	4.59	1.65	0.56
SD	11.99	41.47	32.17	14.48	10.28	1.11	0.49
LW	13.78	41.25	11.92	19.37	25.26	1.62	0.58
HM	11.70	71.03	8.35	7.63	12.24	0.46	0.29

where A is the pre-exponential factor, E is the activation energy, and x is the weight loss fraction or conversion at temperature T or time t, which can be calculated by

$$x = \frac{W_o - W_t}{W_o - W_f} \tag{2}$$

where W_o is the original mass of the test sample, W_t is the mass at time t, and W_f is final mass at the end of combustion. For a constant heating rate H during combustion, $H = dT/dt$, rearranging eq 1 and integrating gives

$$\ln\left[\frac{-\ln(1-x)}{T^2}\right] = \ln\left[\frac{AR}{HE}\left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT} \tag{3}$$

From the plots of $-\ln[-\ln(1 - x)/T^2]$ vs $1/T$ for the four chars in Figure 6, the values of E and A in the main combustion region can be obtained, which are shown in Table 8. The good correlation coefficient indicates that the char combustion reaction can be described by a first-order reaction model. Clearly, the activation energies and pre-exponential factors of the chars from the weakly reductive coals are lower than those of the char from PS coal, suggesting the easy combustibility of those chars, which is quite accordant with the results in Table 7.

The gas products from coal pyrolysis are mainly composed of H_2, CH_4, CO_2, and CO, along with a little C_2H_4 and C_2H_6. The detailed gas compositions from different coal pyrolyses at 650 °C are listed in Table 9. Compared with PS coal, the weakly reductive coals have high CO and CO_2 yields. It is thought that

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the results are related to higher oxygen and carboxyl contents in weakly reductive coals.

4. Conclusions

The weakly reductive coals exhibit pyrolysis behaviors significantly different from that of the reductive coal although they have very similar elemental compositions. From TG/DTG analysis, the weakly reductive coals show obviously lower weight loss and weight loss rate but higher peak temperature than the reductive PS coal, and the weight loss of coal in the main pyrolysis range decreases with increasing inertinite content of coal. From the pyrolysis of coals in a fixed-bed reactor, the weakly reductive coals have lower conversion and tar yield than reductive PS coal in the temperature range studied. The tars from the weakly reductive coals contain more oxygen-containing and aromatic groups and more aliphatic hydrogen at carbon atoms bonded to other aliphatic carbon atoms but lower aliphatic hydrogen adjacent to aromatic alkene groups than that from PS coal on the basis of the data of FT-IR and ^{1}H NMR. The chars from the weakly reductive coals are more reactive and easily burned than that from PS coal. These findings will be helpful for people to understand the difference in pyrolysis behavior between weakly reductive and reductive coals, and the information on coal conversion and properties of products of coal pyrolysis will also be helpful for people to make rational use of these coals.

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