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Application of TG–DTG analysis and centrifugal separation in the investigation of less combustible constituents in coals

Xinqian Shu[a,*], Xuchang Xu[a], Hongli Fan[a], Shen Wang[b], Dezhong Yan[a]

[a]*Department of Thermal Engineering, Tsinghua University, Beijing 100084, PR China*
[b]*Haikou Power Plant Co. Ltd., Haikou, Hainan Province, PR China*

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Abstract

Three coals of Yangquan anthracite (YQ), Huainan bituminous coal with a medium amount of volatile matter and Shenfu bituminous coal with a high amount of volatile matter (SF) are used for the investigation of less combustible constituents (LCC) . It has been concluded that some less combustible constituents exist in coals by means of centrifugal separation (CS) with gravity liquids and thermogravimetric analysis (TG) with a Du Pont-2100 thermal balance. The constituents always lie in the separation fraction with the specific density, which differs from each other in various coals. The LCC in coals always give a lower value of the maximum combustion rate, and also lower kinetic parameters, like activation energy (E) and apparent pre-exponential factor (k_0). © 2002 Published by Elsevier Science B.V.

Keywords: Centrifugal separation with a gravity liquid; Thermogravimetric analysis; Less combustible constituents; Maximum combustion rate; Kinetic parameters

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1. Introduction

Scientists began to pay attention to the existence of some less combustible constituents (LCC) in coals long before. Especially, since Shibaoka [1] firstly noticed differences in the combustion of various materials in the same coal, Nandi et al. [2], Lee and Whaley [3], Shibaoka [4], Jones et al. [5], Morgan et al. [6], Crelling et al. [7,8], White et al. [9], Zheng [10] and Zheng et al. [11] put forward in succession that inertinite was less flammable than other materials in coals. However, further researches revealed that not all inertinites were difficult to burn, just some of them showed slower combustion, i.e. inertinites with higher reflectance. Conventionally, whether a material was flammable or less flammable, was usually determined by its reflectance. However, it is worth mentioning that researchers yet so far have not proposed a generally recognized criterion on the reflectance identification of LCC. Falcon and Snyman [12] thought that LCC was the inertinite with a reflectance of 0.03% above vitrinite. Skorupska et al. [13] considered LCC being the inertinite with a reflectance of 0.5% over vitrinite. Coin and Hall [14] held a viewpoint that the reflectance of LCC was always larger than 2.8%.

Abbreviations: LCC, less combustible constituents; CS, centrifugal separation; TG, thermogravimetric analysis; DTG, the first order of differentiation curve of mass loss to time; YQ, Yangquan anthracite; YQR, Yangquan raw coal; YQV, Yangquan vitrain; HN, Huainan bituminous coal with medium volatile matter; HNR, Huainan raw coal; SF, Shenfu bituminous coal with high volatile matter; SFR, Shenfu raw coal; DTF, drop tube furnace

[*] Corresponding author. Laboratoire Gestion des Risques et Environment, Universite, de Haute Alsace, 25, ruedu Chemnitz, 68200 Mulhouse, France. Tel.: +33-389-327673;
fax: +33-389-327661.
E-mail addresses: sxinq@yahoo.com (X. Shu).

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Nomenclature

D_{max}	maximum devolatilization rate (wt.% min^{-1})
C_{max}	maximum combustion rate (wt.% min^{-1})
A	ash content (wt.%)
V	volatile matter content (wt.%)
E	activation energy (kJ mol^{-1})
k_0	apparent pre-exponential factor (kg m^{-2} s^{-1} MPa^{-1} O_2)

In the meantime, Diessel and Wolff-Fisher [15] and Bailey et al. [16] deduced two different mathematical functions to differentiate fusible and infusible constituents in coals based upon their reflectance, which represented different constituents in combustion. The fact mentioned above indicates that it is not so clear to determine LCC. It is even harder to quantify LCC just by means of reflectance measurement. Therefore, it is necessary to find other feasible ways to accurately determine and characterize LCC in coals.

On the basis of the previous research [17–20], the authors adopt centrifugal separations (CS) and thermogravimetric analysis (TG–DTG) to determine LCC in coals. The results demonstrate that some subjective deviation in the determination of LCC raised by reflectance measurement can be avoided. LCC can be accurately separated and quantified. Further, some kinetic parameters can be determined in combination with a mathematical calculation and numerical imitation. So, it could be more easily and widely applied in engineering and industrial practices.

2. Experimental

2.1. Samples

Three Chinese energy coals of Yangquan anthracite (YQ), Huainan bituminous coal with medium volatile matter (HN) and Shenfu bituminous coal with high volatile matter (SF) were used as samples during the experiments. They differ from each other not only in volatile matter, being 8.61, 26.96 and 33.73%, but also in ash content, being 57.26, 34.28 and 6.92%. This means that the samples used are relatively representative.

2.2. Test

Coals were first separated to various fractions by CS using a gravity liquid with different densities. TG–DTG was then used for each of them to determine LCC. Further, the YQ was burnt in a drop tube furnace (DTF) to verify the results.

2.2.1. CS with a gravity liquid

At first, samples were pulverized to below 90 μm with a ball mill. Then, 8 g of each pulverized coal were weighed and immersed in 60 ml of a gravity liquid with a series of densities [18,19],and then moved to a

Table 1
Results of separation of three coals[a]

YQ			HN			SF		
Separation density (g cm^{-3})	Fraction	Symbol	Separation density (g cm^{-3})	Fraction	Symbol	Separation density (g cm^{-3})	Fraction	Symbol
1.30	−1.30	Y_1	1.30	−1.30	H_1	1.20	−1.20	S_1
1.40	1.30–1.40	Y_2	1.40	1.30–1.40	H_2	1.25	1.20–1.25	S_2
1.45	1.40–1.45	Y_3	1.45	1.40–1.45	H_3	1.30	1.25–1.30	S_3
1.50	1.45–1.50	Y_4	1.50	1.45–1.50	H_4	1.35	1.30–1.35	S_4
1.55	1.50–1.55	Y_5	1.55	1.50–1.55	H_5	1.40	1.35–1.40	S_5
1.60	1.55–1.60	Y_6	1.60	1.55–1.60	H_6	1.45	1.40–1.45	S_6
1.65	1.60–1.65	Y_7	1.65	1.60–1.65	H_7	1.50	1.45–1.50	S_7
1.70	1.65–1.70	Y_8	1.70	1.65–1.70	H_8	1.55	1.50–1.55	S_8
1.855	1.70–1.855	Y_9		+1.70	H_9	1.60	1.55–1.60	S_9
	+1.855	Y_{10}					+1.60	S_{10}

[a] YQ: Yangquan coal; HN: Huainan coal; SF: Shenfu coal.

LDS-10 centrifugal separator to do CS [21]. The revolution speed of the centrifuge was 3000 min^{-1}. The fixation of the density limits for separation was made by tentative tests [22], and changes according to the density or rank of the raw coals. The results of separation of the three coals are listed in Table 1.

2.2.2. TG–DTG analysis

The TG–DTG was done with a Du Pont-2100 thermal balance. The tests include two stages: pyrolysis and combustion. Coal was first pyrolyzed in nitrogen atmosphere. Combustion was then done under air atmosphere. Mass of specimen in each

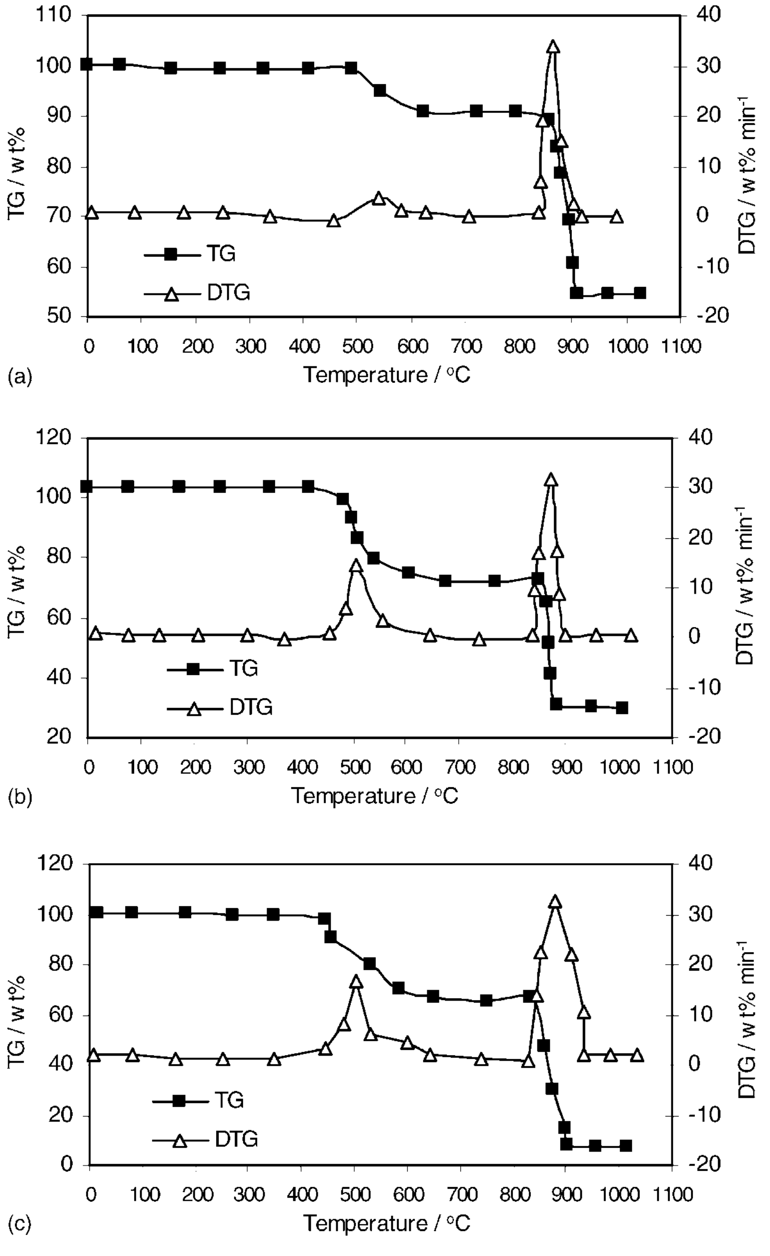

Fig. 1. TG and DTG curves of three coals. (a) YQ; (b) HN; (c) SF.

analysis was about 15 mg. The temperature of the balance rose at rate of 80 K min^{-1}. Gas flow was about 550 ml min^{-1}. Isothermal courses were fixed at temperatures of 160, 950 and 1050 °C during the tests, resulting in the measurement of moisture, volatile matter and ash content respectively. Hereby, the curves of mass loss to temperature (TG) and first order of differentiation curves of mass loss to time (DTG) of the samples were obtained. The characteristic curves of the coals are shown in Fig. 1. It gives three distinctive steps at TG curves, which are related to dewatering, devolatilization and combustion of the coals with the increase of temperature. The DTG curves show two peaks. The first one corresponds to devolatilization of the coals and the second one to combustion of the chars. And the crest values are assigned as the maximum devolatilization rate of the coals ($D_{\max}$) and the maximum combustion rate of the chars ($C_{\max}$) separately.

3. Results and discussions

3.1. Determination of LCC by TG–DTG

Following the above-mentioned test conditions, TG–DTG was done to YQ raw coal (YQR), YQ vitrain

Table 2
Results of TG–DTG of YQ[a]

Sample	Mass (mg)	The values of the second step in TG curve (wt.%)		*A* (wt.%)	$D_{\max}$ (wt.% min^{-1})	$C_{\max}$ (wt.% min^{-1})	*V* (wt.%)
		Initial	End				
YQV	15.63	93.18	92.25	7.35	1.59	38.78	7.75
YQR	15.45	90.33	89.62	52.70	2.79	31.33	10.38
Y_1	15.16	89.84	89.11	8.01	2.11	39.88	10.89
Y_2	15.78	91.94	90.87	5.05	1.52	36.33	9.13
Y_3	15.39	90.91	90.08	4.57	2.05	36.39	9.92
Y_4	15.11	91.29	90.36	5.90	1.90	35.82	9.64
Y_5	15.59	89.71	88.95	23.90	2.09	36.16	11.05
Y_6	15.33	90.89	89.88	9.12	1.80	32.75	10.12
Y_7	15.72	89.73	88.82	45.08	2.22	30.13	11.18
Y_8	15.44	89.49	88.84	54.99	2.76	31.82	11.16
Y_9	15.89	89.33	88.51	60.71	3.06	27.08	11.49
Y_{10}	15.55	90.17	89.68	76.74	3.16	21.88	10.32

[a] $D_{\max}$: maximum devolatilization rate; $C_{\max}$: maximum combustion rate; *A*: ash content; *V*: volatile matter content.

Table 3
Results of TG–DTG of HN

Sample	Mass (mg)	The values of the second step in TG curve (wt.%)		*A* (wt.%)	$D_{\max}$ (wt.% min^{-1})	$C_{\max}$ (wt.% min^{-1})	*V* (wt.%)
		Initial	End				
HNR	15.51	75.82	73.42	35.62	12.79	32.93	26.58
H_1	15.20	66.99	66.20	14.18	19.05	35.05	33.80
H_2	15.52	69.36	68.03	7.81	13.23	37.73	31.97
H_3	15.38	71.39	70.13	11.88	10.69	39.58	29.87
H_4	15.21	76.49	75.55	36.49	10.02	38.44	24.45
H_5	15.50	72.30	71.25	17.20	9.24	39.13	28.75
H_6	15.64	79.74	78.90	48.28	7.07	30.35	21.10
H_7	14.94	72.35	70.53	25.15	13.15	33.92	29.48
H_8	15.32	74.73	73.49	25.32	8.29	34.18	26.41
H_9	15.92	83.59	82.79	70.09	6.05	21.81	17.21

(YQV) and every separation fraction. The results are given in Table 2. In the table, the ash content (*A*) corresponds to the value of the end point in the third step of the TG curve, and the volatile matter (*V*) equals to that 100 minus the value of the end point in the second step of TG curve. The distribution curves of $C_{\max}$, $D_{\max}$, *A* and separation density of YQ are drawn in Fig. 2. It can be concluded that $C_{\max}$ of two fractions in YQ is lower than that of YQR, relating to separation densities of 1.60–1.68 and 1.72 g cm^{-3}; it indicates the existence

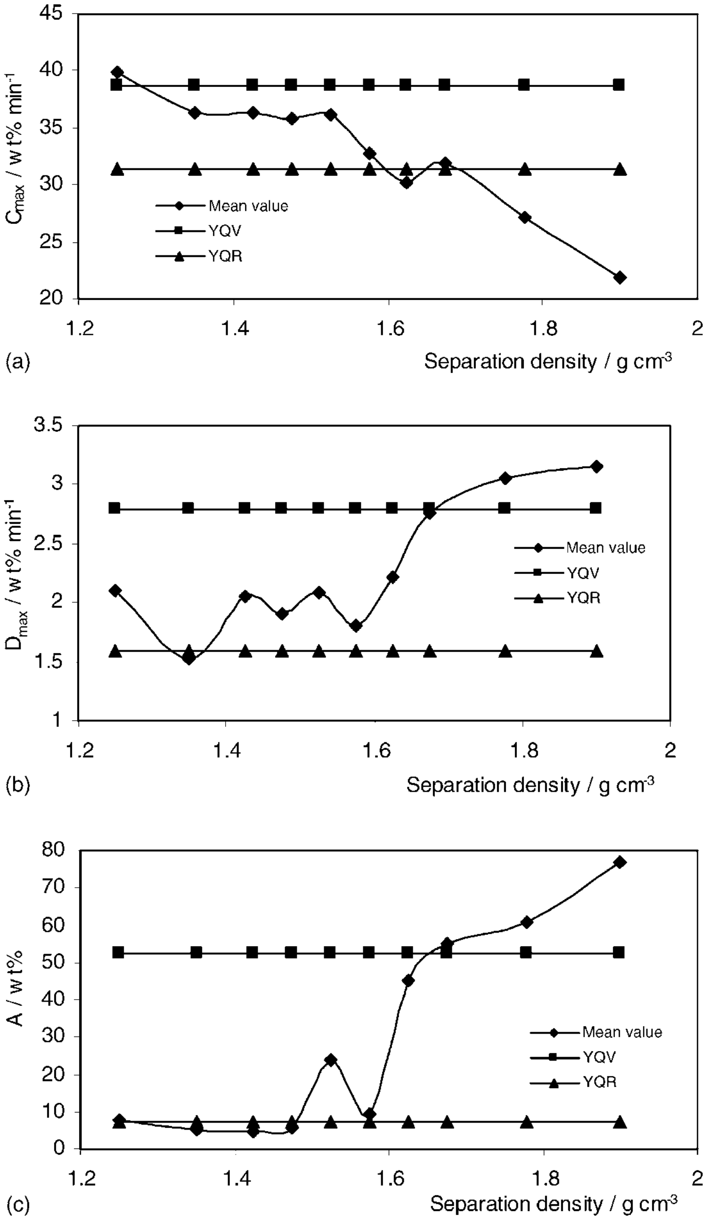

Fig. 2. Distribution of combustion characteristic parameters with separation density in YQ: $C_{\max}$, maximum combustion rate(wt.% min^{-1}); $D_{\max}$, maximum devolatilization rate(wt.% min^{-1}); *A*, ash content (wt.%). (a) Distribution of $C_{\max}$ with separation density in YQ; (b) distribution of $D_{\max}$ with separation density in YQ; (c) distribution of *A* with separation density in YQ.

of LCC in YQ. Moreover, it shows that changes of A and D_{max} of YQ with the increase of separation density are generally opposite to the change of C_{max} with the increase of separation density. This could mean that V of various fractions in YQ is connected with mineral matter (or ash) content in some extent.

Moreover, TG–DTG was done to HN and its separation fractions. Results are shown in Table 3. Curves of C_{max}, D_{max}, and A to separation density are drawn in Fig. 3. It discloses the presentation of LCC in HN. LCC also lies in two fractions, associating with separation densities of 1.56–1.62 and 1.68 g cm^{-3};

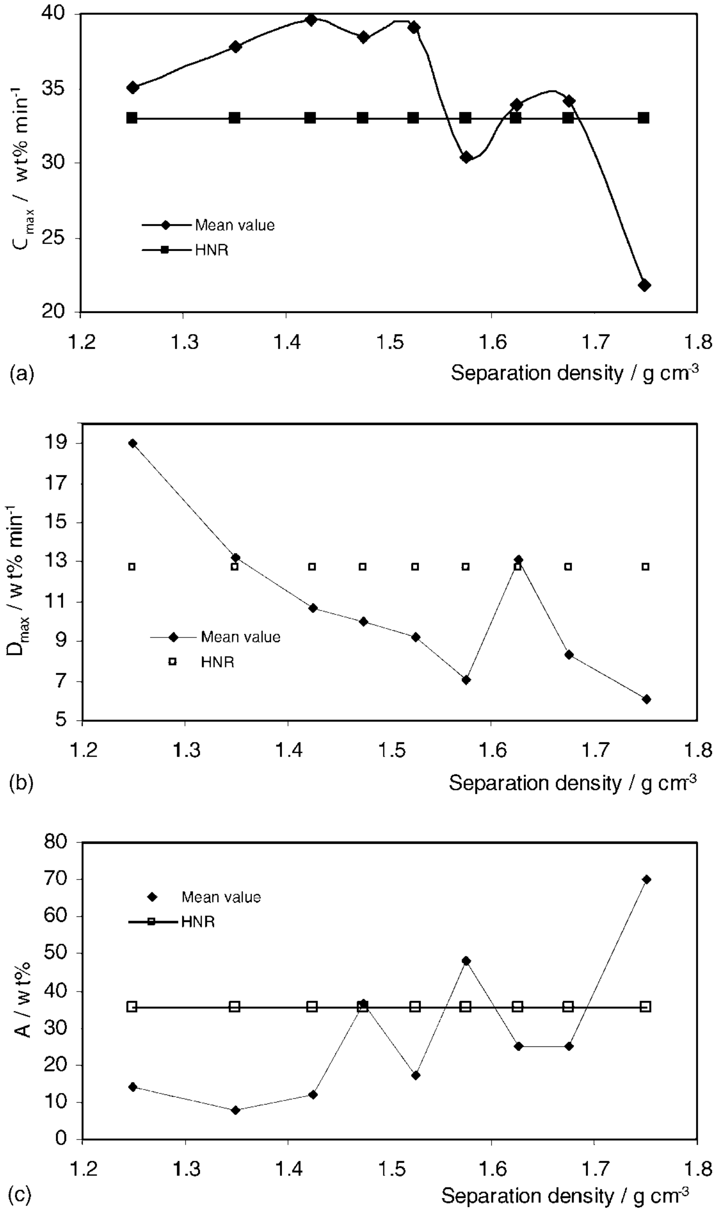

Fig. 3. Distribution of combustion characteristic parameters with separation density in HN: C_{max}, maximum combustion rate (wt.% min^{-1}); D_{max}, maximum devolatilization rate (wt.% min^{-1}); A, ash content (wt.%). (a) Distribution of C_{max} with separation density in HN; (b) distribution of D_{max} with separation density in HN; (c) distribution of A with separation density in HN.

meanwhile, TG–DTG was done to SF and its separation fractions. Table 4 shows the results. Curves of $C_{\max}$, $D_{\max}$, and A to separation density are drawn in Fig. 4. It indicates that LCC in SF is connected to two fractions with densities of 1.46–1.56 and 1.58 g cm^{-3}; in the table and the figure, $C_{\max}$ and $D_{\max}$ of SF basically decrease with the increase of separation densities, while A raises. It demonstrates that V in SF is mainly related to organic constituents or in other words, it has little to do with mineral matters in it.

It should be mentioned that a duplicate test was done to every specimen during the experiments in

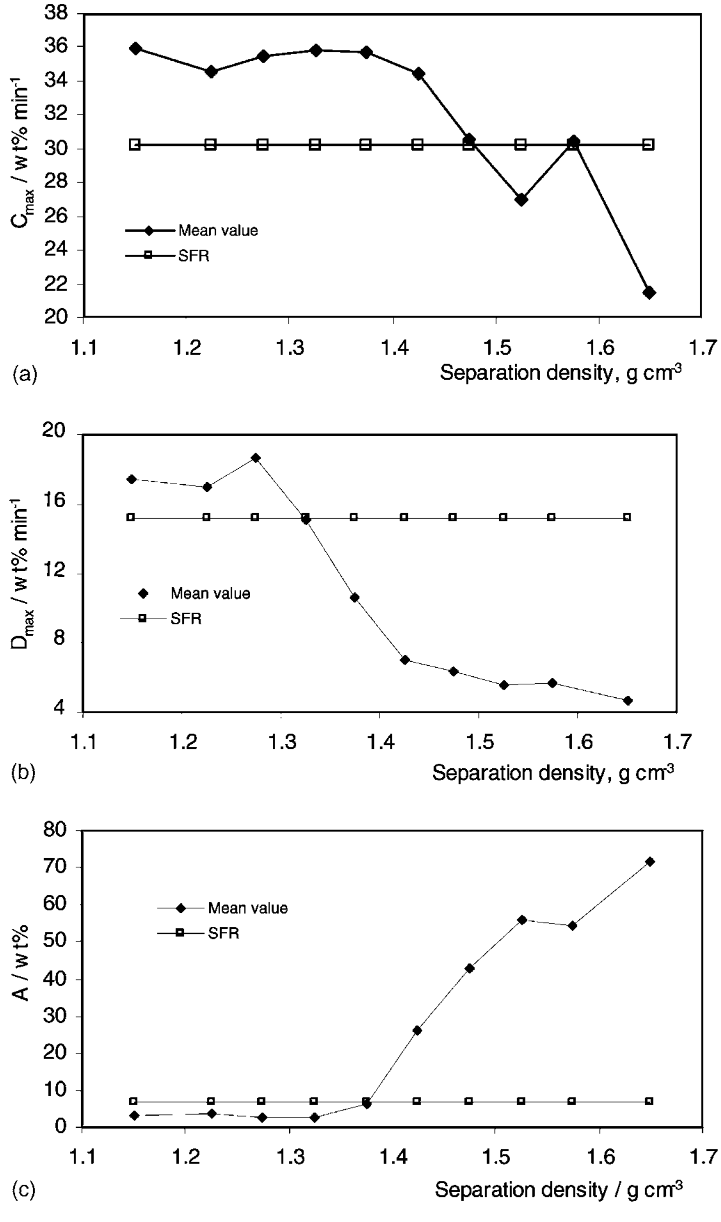

Fig. 4. Distribution of combustion characteristic parameters with separation density in SF: $C_{\max}$, maximum combustion rate (wt.% min^{-1}); $D_{\max}$, maximum devolatilization rate (wt.% min^{-1}); A, ash content (wt.%). (a) Distribution of $C_{\max}$ with separation density in SF; (b) distribution of $D_{\max}$ with separation density in SF; (c) distribution of A with separation density in SF.

Table 4
Result of TG–DTG of SF

Sample	Mass (mg)	The values of the second step in TG curve (wt.%)		A (wt.%)	D_{max} (wt.% min^{-1})	C_{max} (wt.% min^{-1})	V (wt.%)
		Initial	End				
SFR	15.62	67.12	66.11	6.82	15.17	30.25	33.89
S_1	15.04	63.63	62.45	3.27	17.47	35.94	37.55
S_2	15.06	63.79	62.43	3.74	16.99	35.56	37.57
S_3	15.38	61.92	60.42	2.46	18.67	35.52	39.58
S_4	15.36	64.02	62.61	2.36	15.09	35.81	37.39
S_5	15.60	69.43	68.32	6.22	10.56	35.68	31.68
S_6	15.13	77.11	75.98	26.35	6.98	34.50	24.02
S_7	15.57	80.45	79.57	42.75	6.32	30.60	20.43
S_8	15.30	83.42	82.55	55.92	5.57	27.02	17.45
S_9	15.75	81.51	81.34	54.48	5.67	30.99	18.76
S_{10}	15.06	85.68	85.99	71.76	4.68	21.45	14.01

order to make sure that analytical results were accurate and correct. Sometimes, two more analyses had even been carried out when the results were poor in repeatability, such as in the case of YQR [21].

3.2. Verification of LCC by combustion test on a DTF

On the basis of CS and TG–DTG analysis, it is found primarily that there exist some LCC in the coals. Obviously, it is necessary to make a verification by further combustion tests. Accordingly, the authors chose YQR and several separation fractions with densities below 1.60 (YQI), 1.60–1.65 (YQII) and above 1.65 (YQIII) g cm^{-3} and did combustion tests on a DTF in order to substantiate the above results. Meanwhile, kinetic parameters, such as activation energy (E) and apparent pre-exponential factor (k_0) of these samples were further reached in combination with a mathematical calculation and numerical imitation. Test conditions and calculation have been introduced previously [21]. Table 5 shows E and k_0. As seen from it, we conclude that there really exist some LCC in YQ, being in correspondence with the separation density above 1.60 g cm^{-3}, which gives the lower E and k_0.

Table 5
Kinetics of YQ

Samples	E (kJ mol^{-1})	k_0 (kg m^{-2} s^{-1} MPa^{-1} O_2)[a]
YQR	123.43	37.69×10^3
YQI	115.14	30.80×10^3
YQII	63.80	153.48
YQIII	25.59	0.65

[a] The kg m^{-2} s^{-1} MPa^{-1} O_2 for k_0 is because we defined apparent combustion rate as the consumption of chars at the condition of given superficial area, time and oxygen pressure during our experiments and mathematical calculation.

4. Conclusions

To sum up the above mentioned discussions, we can get the following conclusions:

1. There really exist some LCC in coals. LCC always lies in specific separation fractions, corresponding to different separation densities varying with raw coals. For example, LCC in YQ lies in the density range from 1.60 to 1.68 and at 1.72 g cm^{-3}; in HN with the densities from 1.56 to 1.62 and t; 1.68 g cm^{-3}, in SF from 1.46 to 1.56 and t; 1.58 g cm^{-3}.
2. Results obtained indicate that CS and TG–DTG can be used in the determination and investigation of LCC in coals. Particularly, kinetic parameters like E and k_0 can be reached in combination with mathematical calculations. These data could be applied to engineering and industrial practices, such as in the calculation of combustion conditions in the furnaces and in the prediction of unburnt carbons yields in the burners combustion.

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References

[1] M. Shibaoka, Fuel 48 (1969) 285.
[2] B.N. Nandi, T.D. Brown, G.K. Lee, Fuel 56 (1977) 125.
[3] G.K. Lee, H. Whaley, J. Inst. Energy 56 (1983) 190.
[4] M. Shibaoka, Fuel 64 (1985) 263.
[5] R.B. Jones, C.B. McCourt, C. Morley, K. King, Fuel 64 (1985) 1460.
[6] P.A. Morgan, S.D. Robertson, J.F. Unsworth, Fuel 65 (1986) 1464.
[7] J.C. Crelling, N.M. Skorupska, H. Marsh, Fuel 67 (1988)781.
[8] J.C. Crelling, E.J. Hippo, B.A. Woerner, D.P. West Jr., Fuel 71 (1992) 151.
[9] A. White, M.R. Davies, D.D. Jones, Fuel 68 (1989) 511.
[10] Y.S. Zheng, J. Chin. Coal Soc. 15(1990) 80 (in Chinese).
[11] Y.S. Zheng, X.A. Gong, J.Y. Zhang, J. Fuel Chem. Technol. 20(1992) 225 (in Chinese).
[12] R.M.S. Falcon, C.P. Snyman, Review Paper No. 2, Geological Society of South Africa, Johannesburg, 1986.
[13] N.M. Skorupska, A. Sanyal, A. Hesselman, in: Proceedings of the International Conference on Coal Science, Elsevier, Amsterdam, 1987, p. 827.
[14] C.D.A Coin, K.N. Hall, in: Proceedings of the Maceral '89 Symposium, CSIRD Div. Coal Technol., North Ryde, NSW, 1989, pp. 7.1–7.12.
[15] C.F.K. Diessel, E. Wolff-Fisher, in: J.A. Moulijn, et al. (Eds.), Proceedings of the 85; International Conference on Coal Science, Elsevier, Amsterdam, 1987, p. 901.
[16] J.G. Bailey, A. Tate, C.F.K. Diessel, T.F. Wall, Fuel 69 (1990) 225.
[17] X.Q. Shu, Ph.D Thesis of CUMT(Beijing), Beijing, 1995; PR China (in Chinese).
[18] Q.L. Lu, X.C. Xu, D.Z. Yan, J. Fuel Chem. Technol. 21(1993) 273 (in Chinese).
[19] S.C. Wang, Master Thesis of Tsinghua University, Beijing, PR China, 1995; (in Chinese).
[20] H.L. Fan, Master Thesis of Tsinghua University, Beijing, PR China, 1996 (in Chinese).
[21] X.Q. Shu, Postdoctoral Researcher's Report of Tsinghua University, Beijing, PR China, 1997 (in Chinese).
[22] S. Wang, Dissertation of Tsinghua University, Beijing, PR China, 1996 (in Chinese).