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A study of the relationships between the micro-Raman spectral parameters and the combustion characteristics of 32 kinds of Chinese coals

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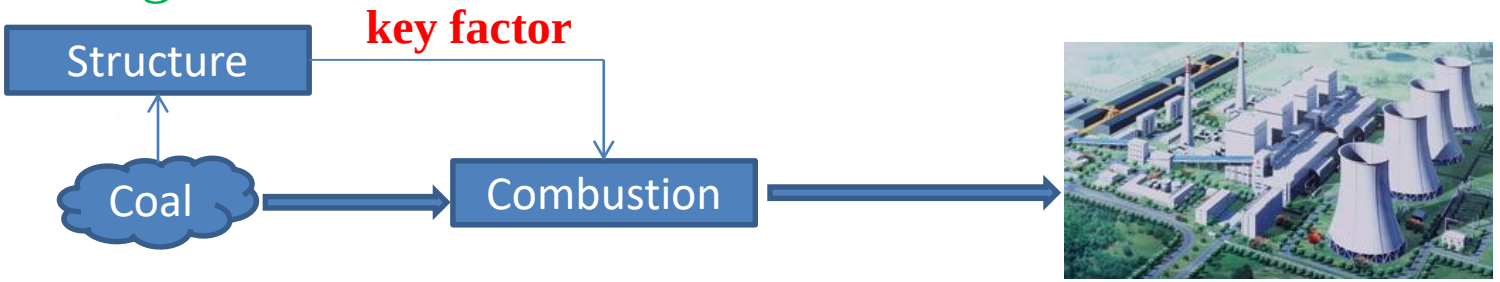
1 BACKGROUND

2 EXPERIMENTS

3 RESULTS & DISCUSSION

4 CONCLUSION

1、Background



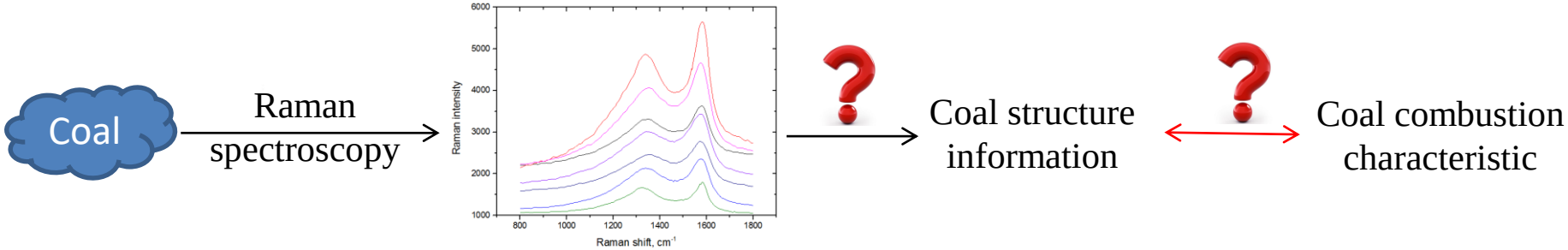
- As coal industry becomes more and more intelligent, rapid or real-time accurate measurement of coal structure is of great interest to the coal industry [1, 2].

Raman spectroscopy：high-efficiency(test in seconds), nondestructive，high-precision, no complex sample preparation [1, 3].

It is considered to be a potential analytical tool to realize online coal analysis [1].

[1] Potgieter-Vermaak S et al. J. Raman Spectrosc 2011; 42: 123-9. [2] Won KM et al. Korean J Chem Eng 2009; 26: 489-95. [3] Sadezky A et al. Carbon 2005; 43: 1731-42.

1、Background

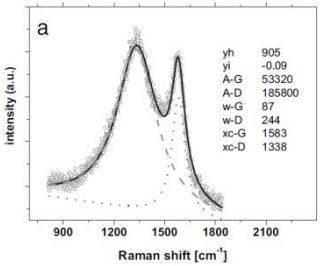


Characteristics: Raman spectrum of raw coal:

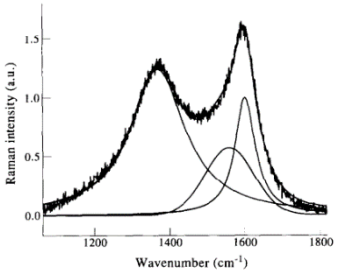
- Two characteristic bands: D band (1340 cm^{-1}) and G band (1580 cm^{-1})(same as graphite-like materials),
- FWHM of G and D bands, the G band and D band position would change regularly with the increase of coal rank [1-3]. But, few detailed structure information has been revealed
- Broad G band and D band, large overlap between G band and D band (Different)

[1] Ulyanova EV et al. Int J Coal Geol 2014; 121: 37-43. [2] Hinrichs R et al. Int J Coal Geol 2014; 136: 52-8. [3] Kelemen SR et al. Energ Fuel 2001; 15: 653-658.

1、Background



Hinrichs R. et al



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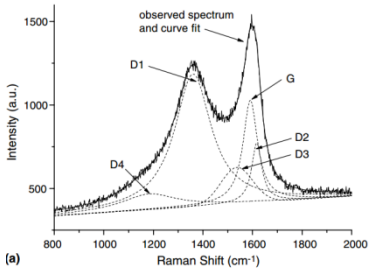
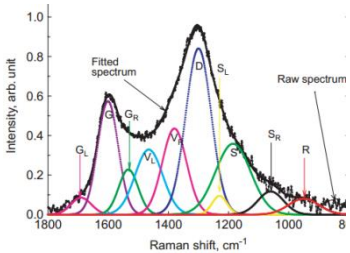


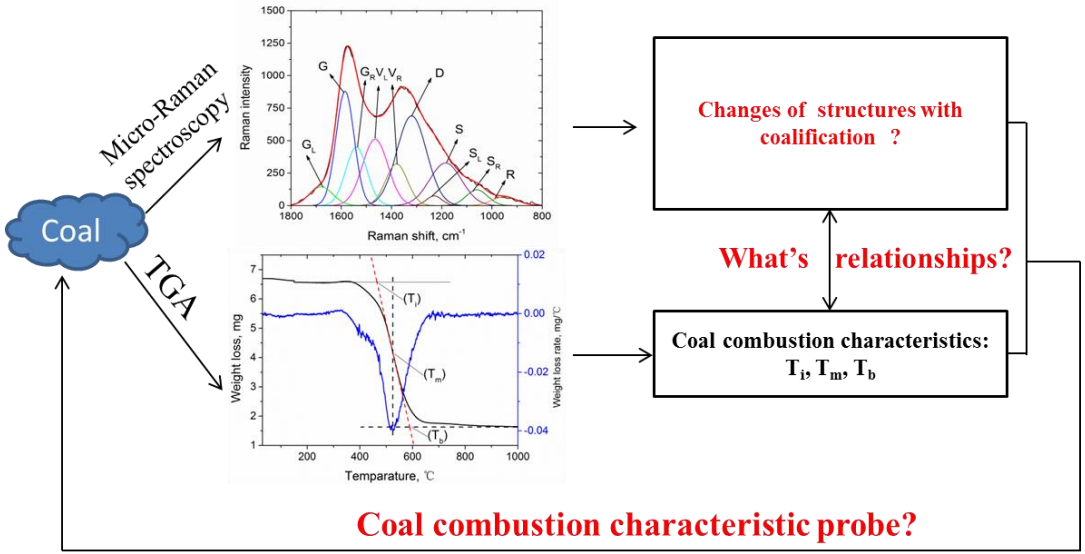
Sadezky A. et al



Li. et al

- More bands exist for poorly ordered carbon materials.
- Detailed structural information can be revealed by deconvolution of the spectrum.
- But rare works have been done for the raw coals with detailed curve-fitting method especially based on large amount samples.
- Moreover, coal combustion characteristics were not correlated to the structures revealed by Raman spectroscopy.

1、Background



Aim of this work:

- Reveal detailed structure information of the raw coals by curve-fitting the Raman spectra based on large amount coal samples.
- Set up the correlations between the Raman spectral parameters and the coal combustion characteristics

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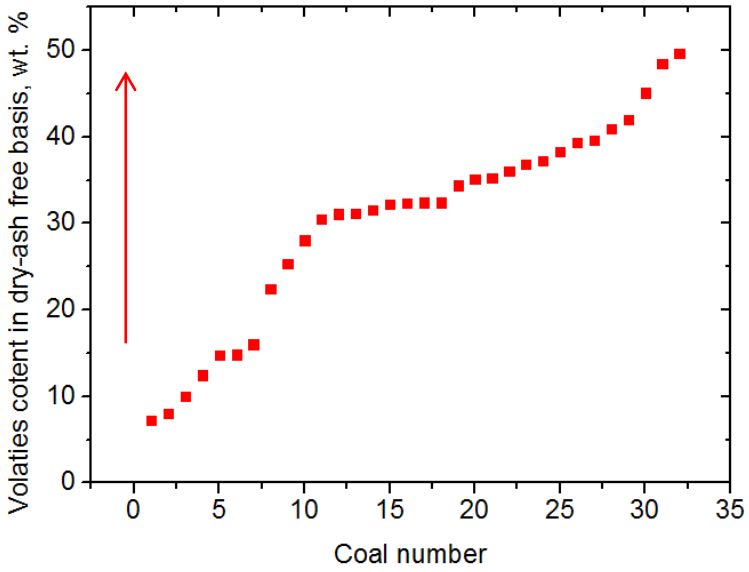
2、Experiments

Coal samples

Fig 1



- Coal samples: 32 kinds of Chinese coals with 74-105 μm, V^{daf} from 6 %~50 %, covering the lignite to anthracite.
- Test state: to keep the coal characteristics in the state of nature, coal in air-dry state in subsequent analysis

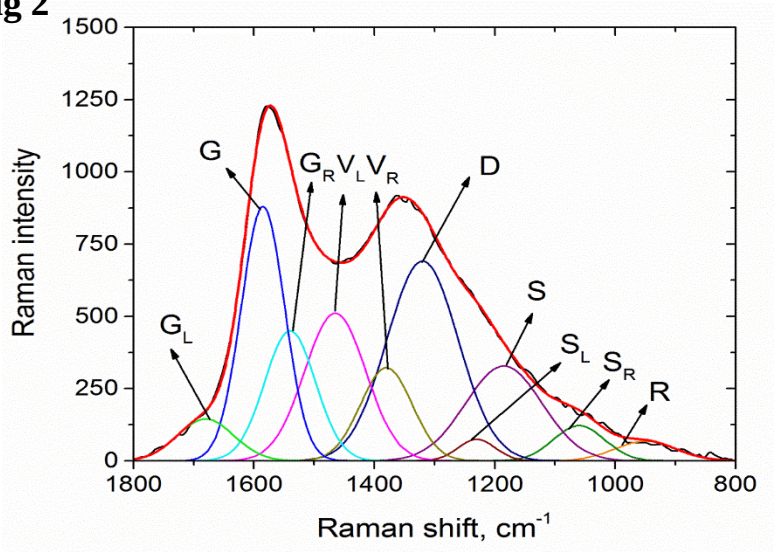
2、Experiments

Raman test:

Micro-Raman spectrometer : Jobin Yvon Lab RAM HR800, Nd-YAG laser (532 nm)

Laser: power 5mW; Beam diameter: 2 μm

Fig 2



- G band: aromatic ring quadrant breathing;
- D band: C-C between aromatic rings, especially aromatics with not less than 6 rings
- (G_R+V_L+V_R) bands: amorphous carbon structures, especially aromatics with 3-5 rings;
- S band: $C_{aromatic}$–C_{alkyl}; aromatic (aliphatic) ethers; C–C on hydro-aromatic rings;
- G_L band: Carbonyl group C=O
- S_L, S_R, R: minor bands and not discussed.

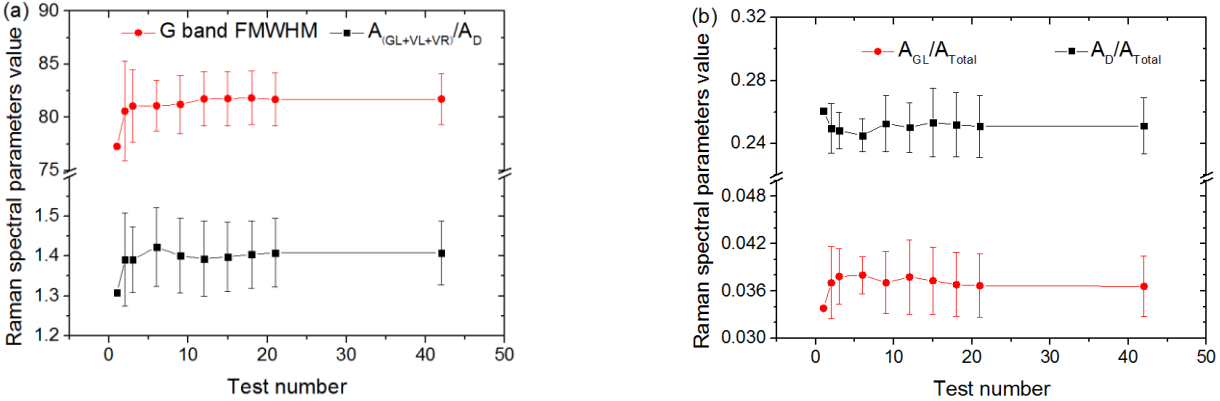
[1] Li X et al. Fuel 2006; 85: 1700-7. [2] Xu .et al. Appl Energy 2016; 182: 20-8. [3] Xu .et al. Energ Fuel 2016; 30: 9071-9.

2、Experiments

Raman test:

Coal is highly heterogeneous, the results may depend on the test position. Average value and standard deviation of the results depended on the test number was evaluated

Fig 3



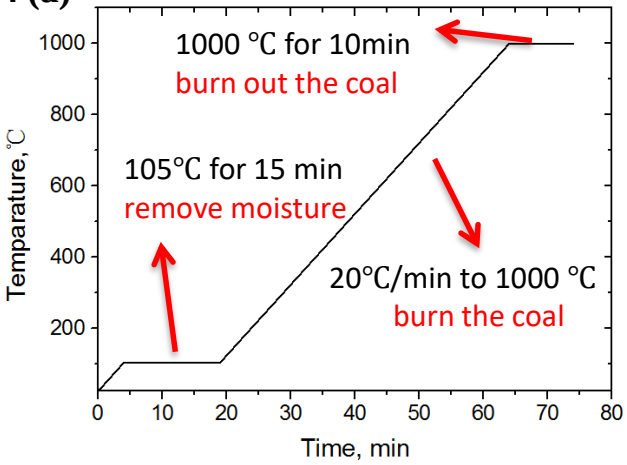
- When the test number is larger than 9, the average value changed little.
- For each sample, 10-15 grains were chose to be tested for each sample to improve the accuracy of the results.

2、Experiments

Combustion test:

Thermo-gravimetric analysis :NETZSCH STA 449 F3, 6.5±0.1 mg for each test.

Fig 4 (a)



2、Experiments

Combustion test:

Thermo-gravimetric analysis :NETZSCH STA 449 F3, 6.5±0.1 mg for each test.

Tangent method [1, 2]:

ignition temperature (T_i)

temperature for the maximum mass loss rate (T_m)

burn out temperature (T_b)

Fig 4 (a)

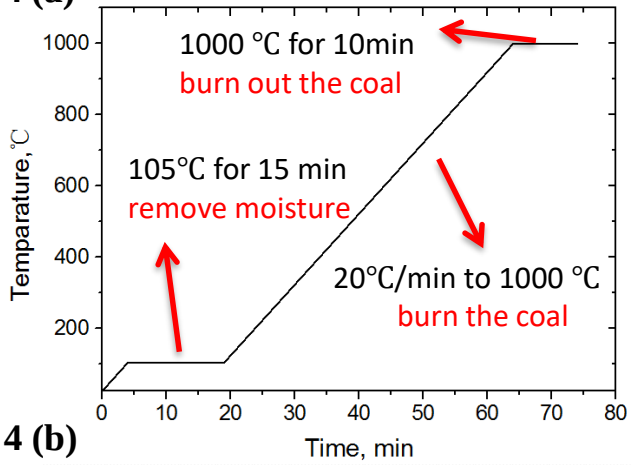
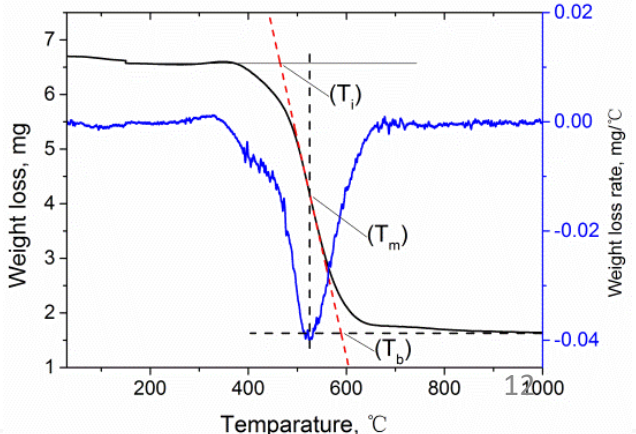


Fig 4 (b)



[1] Zhang et al. J Therm Anal Calorim 2012; 107: 935-42.
[2] Fangxian .et al. J Therm Anal Calorim 2009; 95: 633-8

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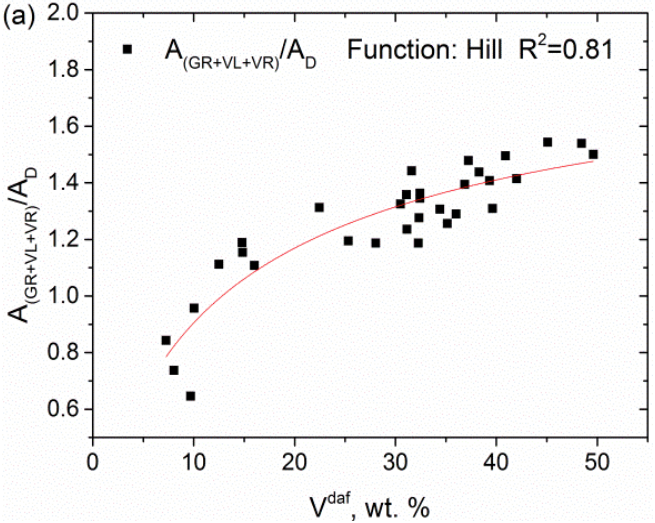
3、Results & Discussion

3.1 Change in structures of the coals with coalification (aromatic rings)

Fig 5



$A_{(GR+VL+VR)}/A_D$ [1-3]: represents the ratio of small aromatic rings(3-5 rings) to large ones (not less than 6 rings), the degree of aromatic ring growth.

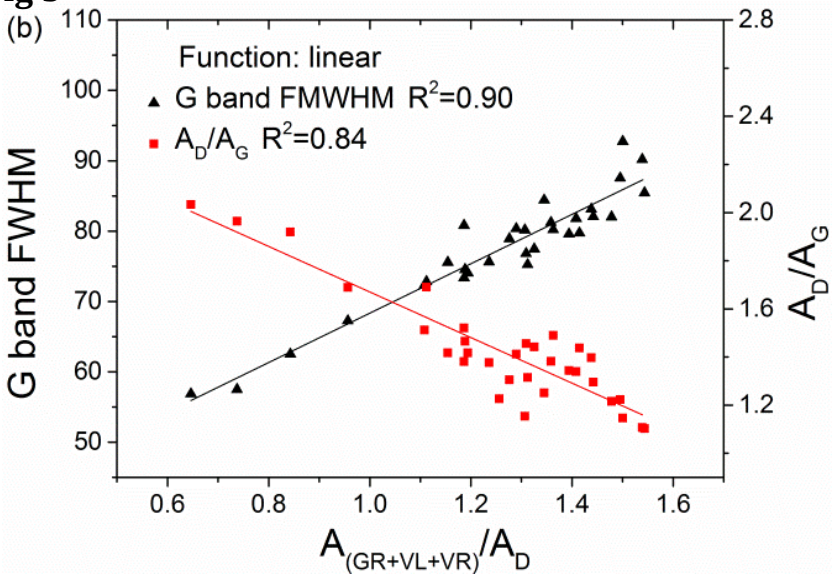
- There will be less relative small aromatic rings but more relative large aromatic rings in the coal with coalification.
- The degree of aromatic ring growth would increase.

[1] Li X et al. Fuel 2006; 85: 1700-7. [2] Xu et al. Appl Energy 2016; 182: 20-8. [3] Xu et al. Energ Fuel 2016; 30: 9071-9.

3、Results & Discussion

3.1 Change in structures of the coals with coalification (aromatic rings)

Fig 5

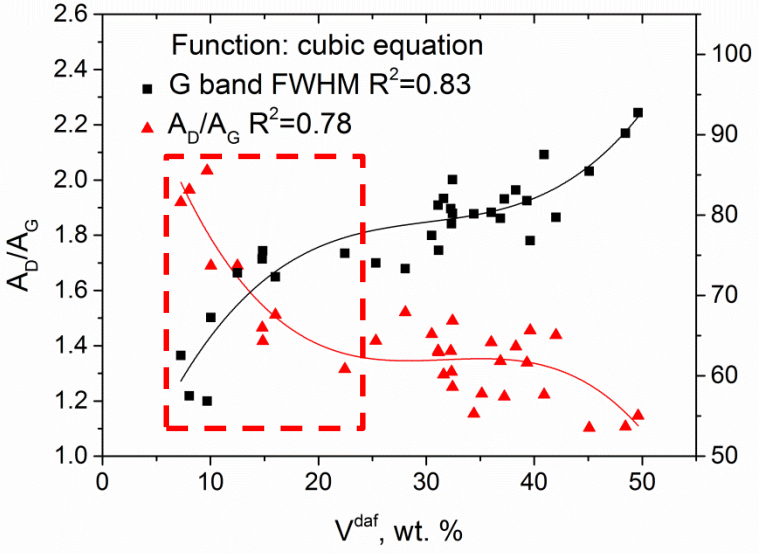


- There are good self-correlations between $A_{(GR+VL+VR)}/A_D$, G band FWHM and A_D/A_G, especially for $A_{(GR+VL+VR)}/A_D$ and G band FWHM.
- G band FWHM : order degree of the aromatic rings, A_D/A_G: relative amount of large aromatic rings.
- They can generally act as the indicators for growth degree of the aromatic rings in the coal.

3、Results & Discussion

3.1 Change in structures of the coals with coalification (aromatic rings)

Fig 6

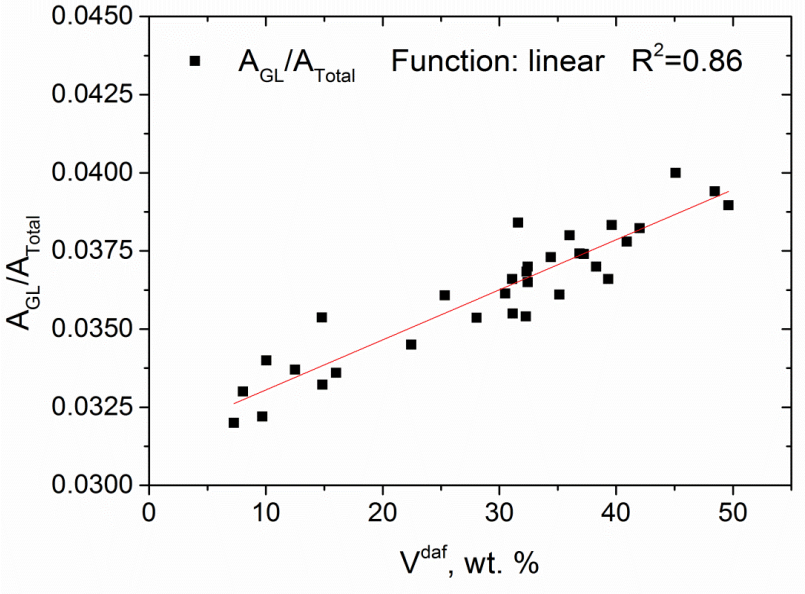


- When $V^{daf} < 25\%$, change drastically indicating rapid growth of the aromatic rings with coalification.
- When $V^{daf} > 25\%$, mildly change with a large dispersion indicating loss of aromatic substituents or aliphatic structures can also take place great probably, and the aromatic rings growth are slow with the coalification.

3、Results & Discussion

3.1 Change in structures of the coals with coalification (O-containing functional group)

Fig 7



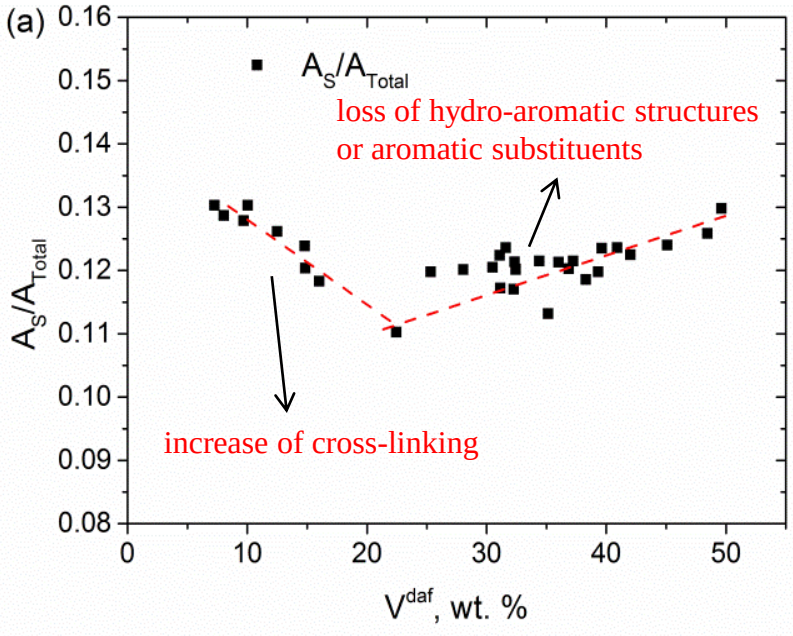
- G_L band mainly represents the carbonyl group C=O in the coal [1-3].
- Nearly linear increase of the A_{GL}/A_{total} with V^{daf} indicates the carbonyl group C=O structures release linearly with coalification.
- Coal rank indicator

[1] Li X et al. Fuel 2006; 85: 1700-7. [2] Xu .et al. Appl Energy 2016; 182: 20-8. [3] Xu .et al. Energ Fuel 2016; 30: 9071-9.

3、Results & Discussion

3.1 Change in structures of the coals with coalification (Cross-linking and aromatic substituents)

Fig 8



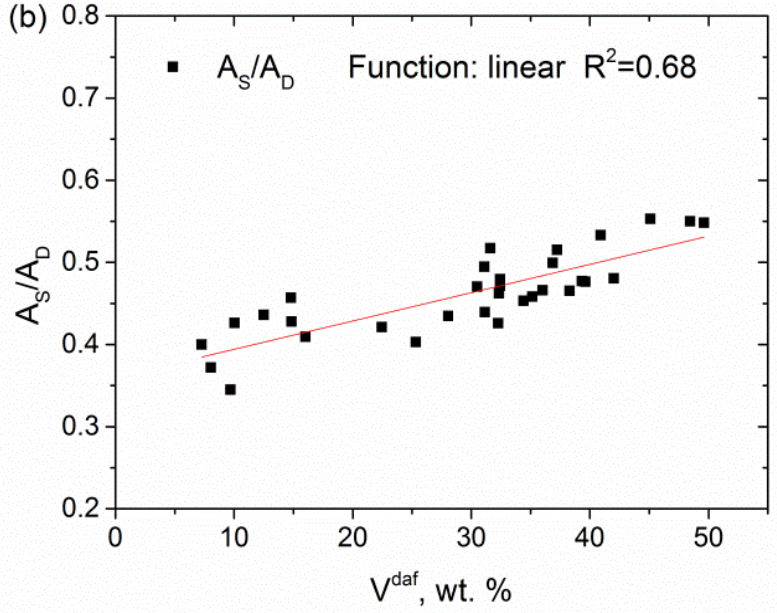
- S band: hydro-aromatic structures as well as the cross-linking $C_{aromatic}$–C_{alkyl} structures and aromatic substituents in the coal [1-3]
- $V^{daf} > 25$ %, mildly decrease of A_S/A_{total} mainly due to the loss of hydro-aromatic structures or aromatic substituents.
- $V^{daf} < 25$ %, rapidly increase suggests the increase of cross-linking $C_{aromatic}$–C_{alkyl} structures with the growth of aromatic rings.

[1] Li X et al. Fuel 2006; 85: 1700-7. [2] Xu et al. Appl Energy 2016; 182: 20-8. [3] Xu et al. Energ Fuel 2016; 30: 9071-9.

3、Results & Discussion

3.1 Change in structures of the coals with coalification (Cross-linking and aromatic substituents)

Fig 8

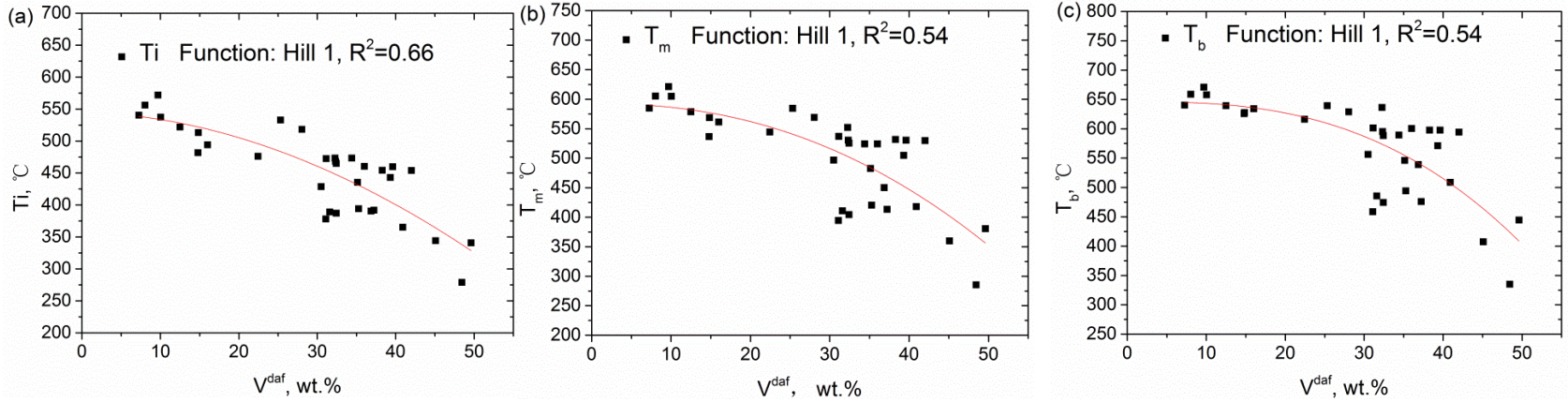


- A_S/A_D : ratio of "impurity" structures such as hydro-aromatic or aliphatic or cross-linking alkyl–aryl C–C structures to large aromatic rings.
- It generally increases with the increase of the V^{daf}, indicating "impurity" ratio also decreases for the relative high rank coal as the large aromatic rings also grow rapidly though the cross-linking structures in the coal increased with coalification.

3、Results & Discussion

3.2 Correlations between V^{daf} and coal combustion characteristics

Fig 9

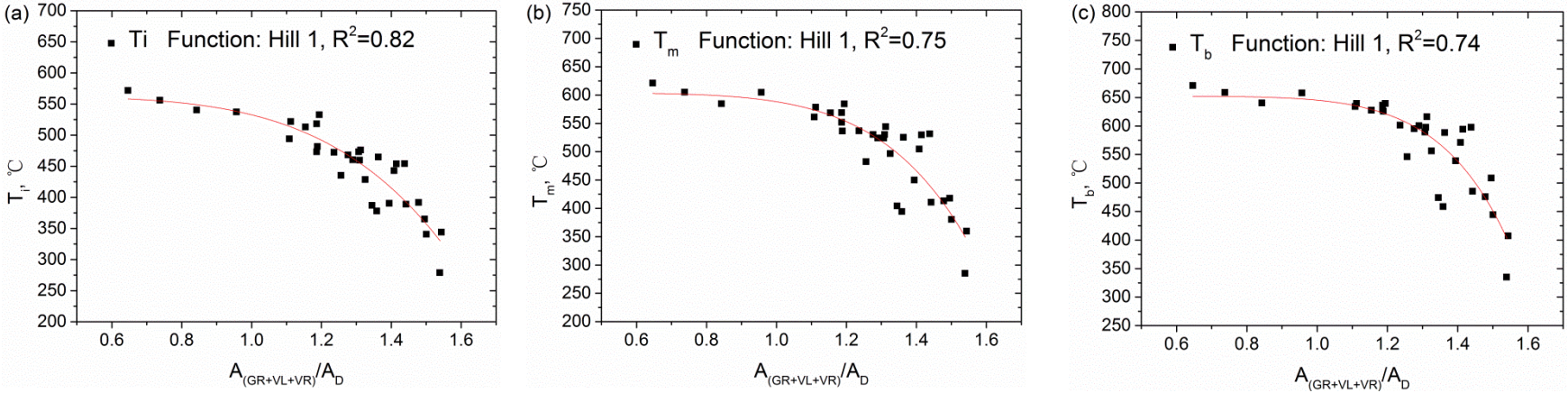


- V^{daf} of the coal can generally reflect the change trend of the coal combustion characteristics, but the accuracy is not high enough especially for the low rank coals as V^{daf} of the coal is only bulk property that cannot accurately describe the detail structures of coal

3、Results & Discussion

3.3 Correlations between Raman spectral parameters and coal combustion characteristic

Fig 10

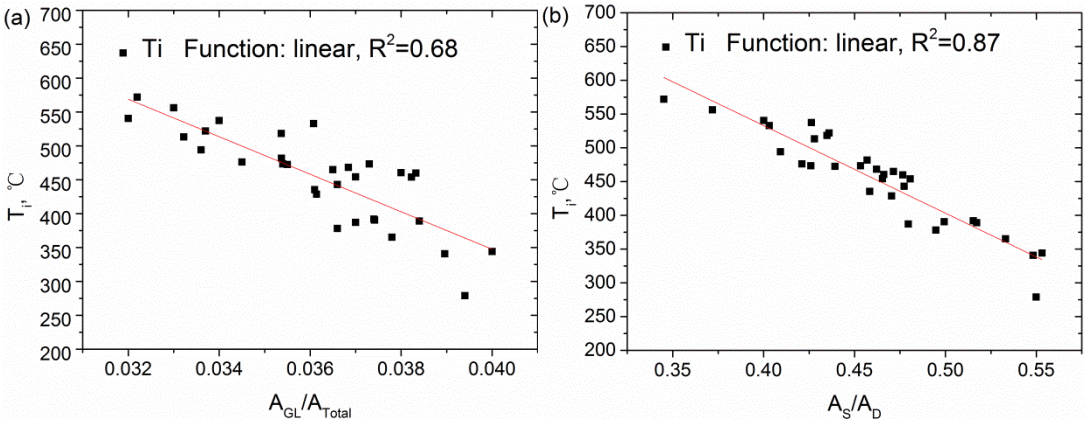


- A coal with higher degree of aromatic ring growth would generally have lower combustion reactivity. When the aromatic ring grows to some extent further increase have little effects on the coal combustion.
- Correlations between the $A_{(GR+VL+VR)}/A_D$ and T_i, T_m, T_b are better than that between V^{daf} and T_i, T_m, T_b

3、Results & Discussion

3.3 Correlations between Raman spectral parameters and coal combustion characteristic

Fig 11



The correlations between T_m, T_b with A_{GL}/A_{Total}, A_S/A_D are similar and not shown.

- The amount of oxygen-containing functional groups and the “impurity” ratio among the large aromatic rings in the coal are also key structures influencing coal combustion characteristics.
- No platform value exists.

3、Results & Discussion

3.3 Correlations between Raman spectral parameters and coal combustion characteristic

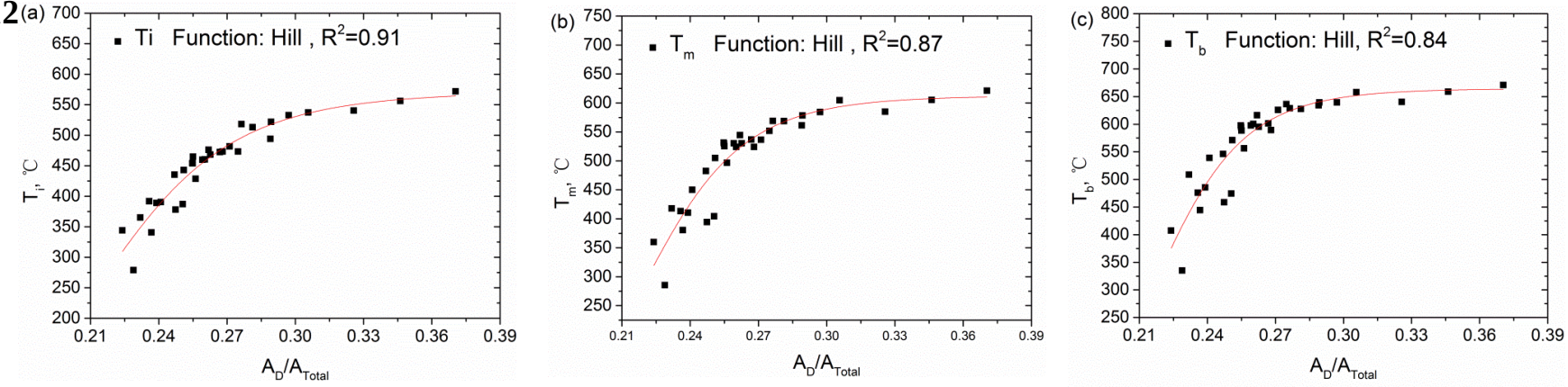
Not only the aromatic rings in the coal but also C=O and “impurity” structures ratio can affect the coal combustion reactivity.

If a parameter can combine them together will be better.

3、Results & Discussion

3.3 Correlations between Raman spectral parameters and coal combustion characteristic

Fig 12



- There are best correlations between the A_D/A_{Total} and T_i, T_m and T_b.
- It seems inconceivable as the relative amount of the large aromatic rings in the coal is not the key factor.

3、Results & Discussion

3.3 Correlations between Raman spectral parameters and coal combustion characteristic

Parameter meaning of A_D/A_{Total} is further analyzed:

$$\frac{A_D}{A_{Total}} = \frac{A_D}{A_{(D+(GR+VL+VR)+G+S+GL+(SL+SR+R))}} = \frac{1}{(1+\frac{A_{(GR+VL+VR)}}{A_D}+\frac{A_G}{A_D}+\frac{A_S}{A_D}+\frac{A_{GL}}{A_D}+\frac{A_{(SL+SR+R)}}{A_D})}$$

- A_D/A_{Total} is actually a combination of $A_{(GR+VL+VR)}/A_D$, A_G/A_D, A_S/A_D, A_{GL}/A_D and $A_{(SL+SR+R)}/A_D$.
- A_D/A_{Total} mainly combines the parameters that represent aromatic rings, C=O structures and the "impurity" structures ratio as the S_L, S_R and R bands are minor bands and $A_{(SL+SR+R)}/A_D$ has limited effects on the value of A_D/A_{total} for different coals.
- A_D/A_{Total} can act as a good indicator for the coal combustion characteristics.

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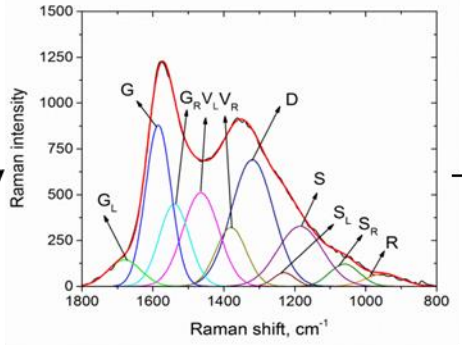
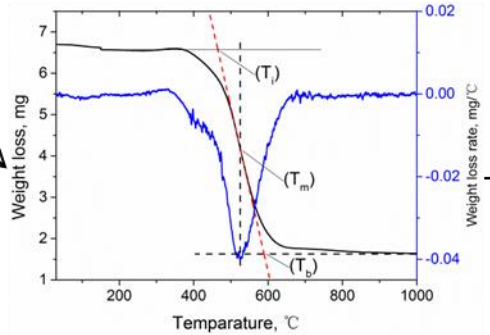
4、Conclusion

Coal

Micro-Raman spectroscopy



TGA



- For low rank coal ($V^{daf}>25\%$), the loss of the aromatic substituents or aliphatic structures more probably takes place with the coalification, while for relative high rank coal ($V^{daf}<25\%$), the growth of the aromatic rings mainly takes place.
- C=O structures nearly increase linearly with the increase of the V^{daf} in the coal.
- The condensation of aromatic rings, loss of C=O structures and reduction of "impurity" ratio all can decrease the coal combustion reactivity.

Reasonable correlations

Coal combustion characteristics:
T_i, T_m, T_b

coal combustion characteristic probe: A_D/A_{Total}

Acknowledgments

- This work was supported by the National Natural Science Foundation of China (NSFC) (Nos.51576081, 51576086, 51576072),
- The national key research and development program of China
- Shanxi Science and Technology Major Project and the Foundation of State Key Laboratory of Coal Conversion (Grant No. J17-18-904).

Thanks for your attention!

Band name	Band position, cm^{-1}	Description
G_L	1700	Carbonyl group C=O
G	1590	Graphite E_{2g}^2; aromatic ring quadrant breathing; alkene C=C
G_R	1540	Aromatics with 3-5 rings; amorphous carbon structures
V_L	1465	Methylene or methyl; semi-circle breathing of aromatic rings; amorphous carbon structures
V_R	1380	Methyl group; semi-circle breathing of aromatic rings; amorphous carbon structures
D	1300	D band on highly ordered carbonaceous materials; C-C between aromatic rings and aromatics with not less than 6 rings
S_L	1230	Aryl–alkyl ether; para-aromatics
S	1185	$C_{aromatic}$–C_{alkyl}; aromatic (aliphatic) ethers; C–C on hydro-aromatic rings; hexagonal diamond carbon sp^3; C–H on aromatic rings
S_R	1060	C–H on aromatic rings; benzene (ortho-di-substituted) ring
R	960-800	C–C on alkanes and cyclic alkanes; C–H on aromatic rings