THE QUANTUM CHEMISTRY STUDIES ON THE THERMOCHEMISTRY OF COAL MODEL COMPOUNDS

Wang Baojun, Zhang Riguang, Ling Lixia

Key Laboratory of Coal Science & Technology, Ministry of Education and Shanxi Province, Taiyuan University of Technology
Taiyuan, 030024, China

Introduction

The calorific power of coal is one of the most important qualities in coal thermochemistry [1]. A number of experimental data on caloric power have been accumulated in previous researches [2,3], and some relevant empirical and semi-empirical calculation formulas were put forward to describe the properties of thermochemistry (most of which is combustion caloric power) of coal with different coal ranks [4].These research results mainly focus on accumulation and classification of experimental data and the fitting of empirical formula. Meanwhile, for coal model molecule, the lack of information on the experimental and theoretical date about molecule rotation and vibration et al makes it difficult to obtain free degree distribution function. As a result, we also can't work out the thermodynamic function using statistical method. However, this problem can be well dealt with by using quantum chemistry calculation method, which can easily provide a number of thermodynamic parameters, for example, entropy S^0, enthalpy H^0 and Gibbs free energy G^0 including the contribution of molecule rotation, vibration, translation and so on.

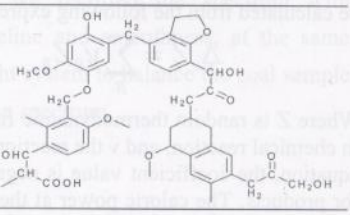
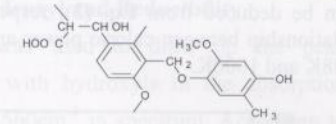
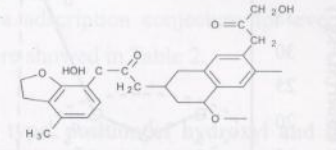
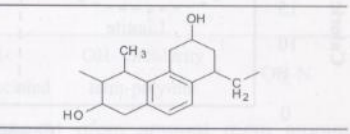
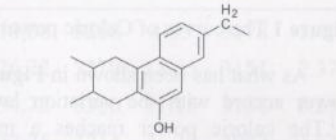
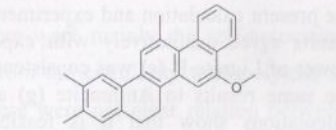
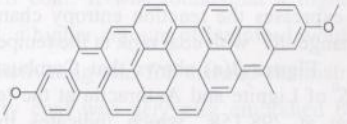
In this paper, we have employed density function theory to investigate the properties of thermochemistry of coal model compounds with different coal rank, and to understand comprehensively their thermodynamic nature.

Models of Coal and Computational methods

The choice of coal model. In this paper, nine structure unit of five types of coal with different coal rank were chosen, which is lignite, subbituminous coal, high volatile bituminous coal, low volatile bituminous coal and anthracite[5]. The nine structure units and their molecular formula were shown in **Table 1**. For lignite model **(a)**, we try to decrease the atom number of its model structure on the principle of keeping its chemical structure characteristics, and to cut off the model from the methylene position, where it have little effect on electron distribution and don't connect with other functional group. Then, the rupture position is saturated by hydrogen, in result, two model molecules are formed: Lignite-L **(b)** and Lignite-R **(c).** For Anthracite **(g)**, we cut down the number of aromatic cycle to form model molecule Anthracite-S **(i).** Because of a small proportion of N, S heteroatom in Coal, which have little effect on thermal chemical qualities of coal, so we don't consider N, S heteroatom in coal model structure.

Computational methods. The description of coal thermochemistry qualities with different coal ranks were given out by using density function theory (DFT) method. The high efficient computational method and parameters were chosen. The computation task of Optimization & Frequency is carried out on every coal model compounds by Local Density Approximation (LDA) method using Perdew-Wang-Ceperley functional (PWC) and MIN basis set. To obtain more precise estimates of thermodynamic parameters, Zero Point Vibrational Energies (ZPVE) was taken into account. All the calculations were performed using the Cerius^2 program package.

Table 1 The coal structure units with different coal rank

Coal species	Structure unit
Lignite $C_{42}H_{44}O_{13}$ **(a)** (Saturated by hydrogen)	
Lignite-L $C_{18}H_{20}O_7$ **(b)** (Saturated by hydrogen)	
Lignite-R $C_{25}H_{28}O_6$ **(c)** (Saturated by hydrogen)	
Subbituminous Coal **(d)** $C_{18}H_{26}O_2$ (Saturated by methyl)	
High volatile bituminous coal **(e)** $C_{18}H_{22}O$ (Saturated by methyl)	
Low volatile bituminous coal **(f)** $C_{26}H_{24}O$ (Saturated by methyl)	
Anthracite $C_{42}H_{20}O_2$ **(g)** (Saturated by hydrogen) $C_{44}H_{24}O_2$ **(h)** (Saturated by methyl)	
Anthracite-S $C_{26}H_{14}O_2$ **(i)** (Saturated by hydrogen)	

Results and Discussion

Caloric power of combustion reaction. By Optimization & Frequency calculation, the total energy E_e and thermodynamic parameters enthalpy H^0 entropy S^0, and Gibbs free energy G^0 can be provided. The caloric power of coal model compounds can be obtained by reaction enthalpy change $\triangle H_r$ in the following reaction **Eq.(1)**, the reaction enthalpy change, $\triangle H_r$, represents the difference between the enthalpy of products and the reactant.

$$C_mH_nO_p+\left(m+\frac{1}{4}n-\frac{1}{2}p\right)O_2 \rightarrow mCO_2+\frac{1}{2}nH_2O(g) \qquad (1)$$

Where m, n, p is the C, H, O atom number corresponding to every coal model structure, respectively, as shown in **Table 1**.

The random thermodynamics parameters in chemical reactions can be calculated from the following expression:

$$\Delta_r Z = \sum_B \nu_B Z_B \qquad (2)$$

Where Z is random thermodynamic function, B the species involved in chemical reaction, and ν the reaction species coefficient in reaction equation, the coefficient value is negative for reactants and positive for products. The caloric power at the temperature 298K and 1000K can be deduced from **Eq. (2)**, respectively. **Figure 1** presents the relationship between caloric power and coal rank at the temperature 298K and 1000K.

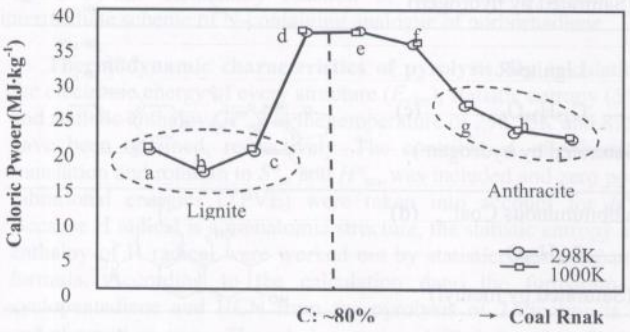


Figure 1 The curves of Caloric power with different coal rank

As what has been shown in **Figure1**, the change trend of caloric power accord with the variation law of coal common properties [6].The caloric power reaches a maximum at about 80% of C content(**C: ~80%**). From the comparison of caloric power between the present calculation and experiment, it is seen that the calculation results agree qualitatively with experimental data [7]. The caloric power of Lignite-R **(c)** was consistent basically with Lignite **(a)**, and the same results to Anthracite **(g)** and Anthracite **(h)**. The above calculations show that it is feasible for simplified coal model structure molecule to calculate caloric power.

Thermodynamic parameters of combustion reaction. Figure 2 expresses the reaction entropy change ΔS and Gibbs free energy change ΔG^0 with coal rank at the temperature 298.15Kand 1000K.

Figure 2(a) shows that Combustion Reaction entropy change ΔS^0 of Lignite and Anthracite at the temperature 1000K is less than that at 298.15K, which indicates the combustion reaction trend increases with the increasing of reaction temperature. However, the ΔS^0 of other coal rank is similar to usual combustion reaction, the temperature have little effect on their reaction trends.

Reaction entropy ΔS^0 of coal model compounds with **C** content about **80%** is greater than that of Young and Old coal rank. From the point of entropy function, It shows that high trend of combustion reaction occur to coal of this coal rank with **C** content about **80%**.

Figure 2(b) gives that Combustion Reaction Gibbs free energy change ΔG^0 of Lignite and Anthracite at the temperature 1000K is less than that at 298.15K, which indicates the isothermal and isotonic combustion reaction has high reaction trend at high temperature. Combustion reaction trend of coal with different coal rank increases with the increasing of reaction temperature, but the argument extent of reaction trend with low rank coal exceeds that of high rank coal. Reaction Gibbs free energy change ΔG^0 of coal model compounds with **C** content about **80%** is less than that of low and high coal rank. From the point of Gibbs free energy function, It can show that high trend of combustion reaction occur to coal of this coal rank with **C** content about **80%**.

The reaction ΔS^0 and ΔG^0 of Lignite-R **(b)** was also consistent basically with Lignite **(a)**, and the same results to Anthracite **(i)** and Anthracite **(g)**, which show that it is believable for simplified coal model structure molecule to calculate thermodynamic function.

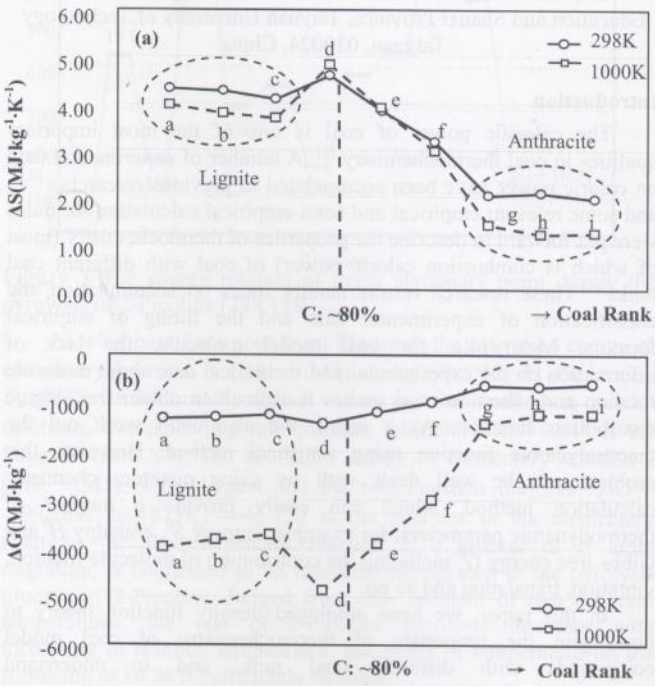


Figure 2 The curves of reaction ΔS and ΔG with different coal rank

On the whole, Coal model compounds at coal rank close to subbituminous coal with **C** content about **80%** have high caloric power and combustion reaction trend.

Acknowledgements

This work was supported by the National Basic Research Program of China (No. 2005CB221203) and the National Natural Science Foundation of China (No.20476069, 20576087) and the Foundation of Shanxi Province (No.2006011022).

References

[1] Xie K. C. Coal Structure and Its Reactivity. Beijing: Science Press, 2002, 27

[2] Chen W. M. Coal Caloric Power and Its Calculation Formula (2nd edition). Beijing: Coal Industrial Press, 1993, 89

[3] Lu Y. K. Acetylene Production from Coal in Plasma Pyrolysis and Analysis of Thermodynamics and Kinetics (Dissertation). Taiyuan University of Technology, 2003, 68-73

[4] Yu J. Y. Coal Chemistry. Beijing: Metallurgy Industrial Press, 2000, 61

[5] Xie K. C. Coal Structure and Its Reactivity. Beijing: Science Press, 2002, 89

[6] Chen W.M. Coal Caloric Power and Its Calculation Formula(2nd edition). Beijing: Coal Industrial Press, 1993, 39

[7] Xie K. C. Coal Structure and Its Reactivity. Beijing: Science Press, 2002, 29