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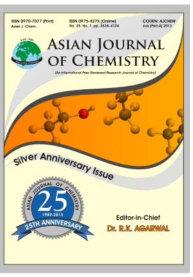

# Effect of Oxidation at Low Temperature on Thermal Dynamics Activation Energy of Lignite†

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In this paper, on the basis of the effect of natural oxidation of lignite in air on coal characters, TG-DSC was performed to analyze oxidation stages and thermal dynamic parameters of original and naturally oxidized for different time lignite. The results showed the TGA and DSC curves of coal samples with low metamorphosed degree testified the five stages during lignite oxidation at low temperature and change of curves at characteristic spots reflected physical adsorption, chemical adsorption and process of chemical reaction and molecular structural conversion in coal. In comparison to that of original coal samples, the dynamics was discussed in different transformation ratio region and mechanism function and thermal dynamic parameters of oxidization pyrolysis process of coal were worked out through Coats Redfern integral method. The activation energy of lignite is low to -27.439 kJ/mol, resulting in coal samples were easy to be oxidized and after oxidation it could be increased by 39.07 kJ/mol. The above finding revealed that the oxidized lignite needed more energy to get to activated state.

**Key Words: Low temperature oxidation, Lignite, Thermal dynamics, TG-DSC, Activation energy.**

## INTRODUCTION

Lignite, a low-rank coal, is liable to influence the low temperature oxidation, leading to great change of coal characters such as oxidization at room temperature, even spontaneous combustion at feasible condition. Coal spontaneous combustion under mine contributes to the gas explosion and severely threatens the safety of production. In addition, also, coal spontaneous combustion does great damage to our environment[1]. However, the reason resulted in the occurrence of above-mentioned mischance has, so far, not been found. So, there is of significant importance to investigate the oxidization of lignite.

Coal spontaneous combustion mainly caused by caloric that release resulting from lignite oxidization in air. The most elementary parameters of reaction property of coal with oxygen were described as burning dynamic parameters. In the burning dynamic parameters, the activation energy represents the absorbed energy of reactants from initial stable state to active molecules. In fact, it much more essentially describes the fire performance of coal than ignition temperature[2]. Therefore, thermal analysis kinetic method aims at understanding of the oxidation mechanism of coal and working out the mechanism function and dynamic parameters of coal oxidation process, providing the theory basis for coal oxidation at low temperature.

## EXPERIMENTAL

Coal samples were tertiary lignite from Tong Liao, Inner Mongolia. Coal samples were divided into two proportions. One as fresh sample was packaged by three layers with black plastic bag in order to prevent natural oxidation. The other as oxidized sample was placed in the open air for 60 days.

Naturally oxidized coal was sampled from the surface of samples, but fresh coal was sampled from the center of samples. A certain amount of two kinds of analyzed samples were taken to grind as powder with lower than 0.15 mm in diameter and then were analyzed using thermogravimetric analyzer (TG209, Netzsch, German).

**Experimental conditions:** In order to obtain TG-DSC curves of coal samples, the operating condition of apparatus was prescribed as follows: resolution was 0.1 μg, air mass flow was 20 mL/min, the heating rate was 10 K/min, temperature range was from room temperature (RT) to 800 ºC, concentration of oxygen was 21%.

## RESULTS AND DISCUSSION

**TG-DSC analysis of lignite:** TG curve reflects the change of coal mass during coal oxidation and temperature rise process and DSC curve reflects the correlation of complexation rate between coal and oxygen with production rate of gas. The

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change of coal mass is caused by combination of coal and oxygen as well as desorption of varieties of gas. Fig. 1 (a) and (b) were the TG-DSC analysis curves of original and oxidized coal samples, respectively. It can be seen that two curves had the same change trend, difference lay in the different decline slope and characteristic temperature of curves. In comparison to the TG-DSC curves of original and oxidized coal samples, the decline of TG curve of original coal samples is greater than that of oxidized ones at the same heating rate and there was a little peak on DSC curve for original coal samples at the range of RT to *ca.* 110 ºC, while TG curve was dropping down, which was caused by the weightlessness arousing from evaporating the moisture. Compared with the original coal samples, oxidized ones reduced much more moisture, which revealed coal samples tend to loose moisture after low temperature oxidation and after oxidation, coal samples had higher ignition temperature and stronger inertia. It can be seen from DSC curves phenomenon of caloric absorption was observed duo to the need of absorbing caloric for the evaporation of moisture. The temperature range from 110 to 300 ºC was defined as weight increasing stage, which was caused by absorption of oxygen and since that, weightlessness of coal samples with high speed happened. When temperature was over 300 ºC, the heated coal samples began to decompose and absorbed caloric, producing a heat absorption peak on DSC curve. At 400 ºC (ignition temperature of coal samples), coal samples took fire. At 400-600 ºC of burning stage. The coal samples burned exquisitely and large amount of caloric was then released, producing a strong caloric release peak on DSC curves. At 600 ºC, coal samples got to complete combustion. The above different stages were the five stages of combustion process of coal samples.

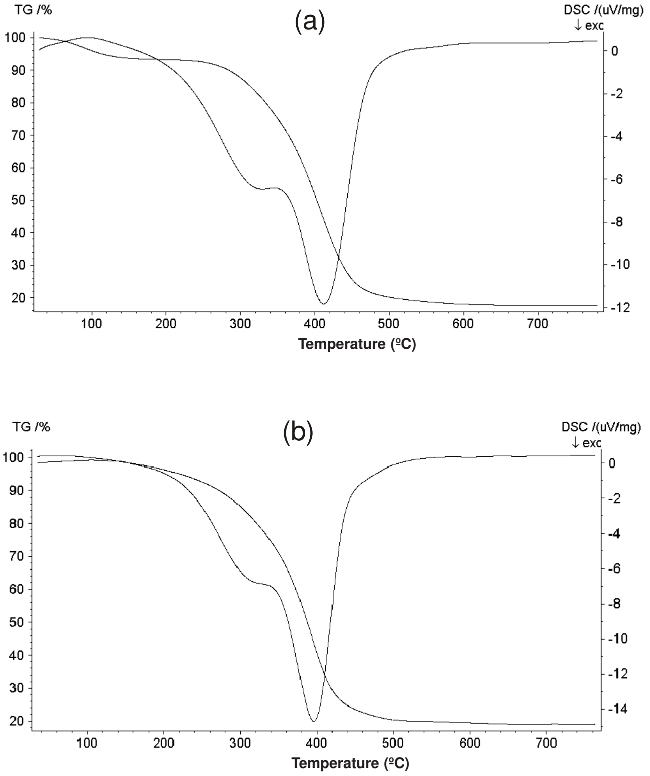

Fig. 1. TG-DSC analysises of original (a) and oxidized coal samples (b)

**Solution of integral function of oxidation thermal pyrolysis dynamics:** In general, Coats-Redfern integral and Freeman-Carrol differential methods were employed for the calculation of activation energy. The latter needs to use some parameter with low precision of reaction process of coal samples. Therefore, Coats-Redfern integral method was utilized as the calculation method for activation energy of coal samples[3].

According to the TG curve, "a" was defined as reaction conversion ratio of coal samples and written as:

$$a = \frac{(m_0 - m)}{(m - m_\infty)} \qquad (1)$$

where $m_0$ and $m_\infty$ are the original and final weight of coal samples, respectively and m is the not reacted one at "t" moment, the decomposition ratio was written as

$$da/dt = kf(a) \qquad (2)$$

where k is the ratio constant. According to the Arrhenius equation:

$$k = Ae^{-E/RT} \qquad (3)$$

where A and E are the frequency factor and activation energy, respectively. R is molar gas constant. Function f(a) rests the reaction mechanism. Toward a simple reaction:

$$f(a) = (1-a)^n \qquad (4)$$

According to the chemical reaction kinetics principle, the reaction rate of coal samples can be written as:

$$da/dt = Ae^{-E/RT}(1-a)^n \qquad (5)$$

At $\beta = dT/dt$ of constant heating rate:

$$da/dT = \frac{A}{\beta}e^{-E/RT}(1-a)^n \qquad (6)$$

It was simultaneous integral for left and right sides of equation 6 at range of 0-a and $T_0$-T, respectively, then:

$$\int_0^a \frac{da}{(1-a)^n} = \frac{A}{\beta}\int_{To}^{T} e^{-E/RT}\,dT \qquad (7)$$

In the case of the left:

$$g(a) = \int_0^a \frac{da}{(1-a)^n} = -\ln(1-a), n = 1 \qquad (8)$$

$$g(a) = \frac{1-(1-a)^{1-n}}{(1-n)}, n \neq 1 \qquad (9)$$

where g(a) is the integral function for TG curve. Different reaction mechanism is corresponding to different dynamic integral function. Ever since, researches on coal combustion mechanism have attracted more and more interest of many scholars. in order to calculate conveniently, Researchers[4-7] described combustion reaction as first order one, then:

$$n = 1, g(a) = -\ln(1-a) \qquad (10)$$

Using Coats-Redfen integral equation[4-7]:

$$\ln\frac{-\ln(1-a)}{T^2} = \ln[\frac{AR}{\beta E}(1-\frac{2RT}{E})] - \frac{E}{RT} \qquad (11)$$

**Effect of low temperature oxidation on dynamic activation energy:** According to equation 11, when a and T values are chosen from selected different temperature region, for certain a reaction series n, given the plot of the ln $[g(a)/T^2]$

*versus* 1/T is linear, then slope of the line obtained is -E/R and frequency factor A is included in intercept of the line obtained. Therefore, activation energy E and frequency factor A are gained. In the present work, Fig. 2 shows the fitted lines of corresponding data of intial and oxidized coal samples, the activation energy E and frequency factor A shown in Table-1 were worked out through the slope and intercept of fitted lines.

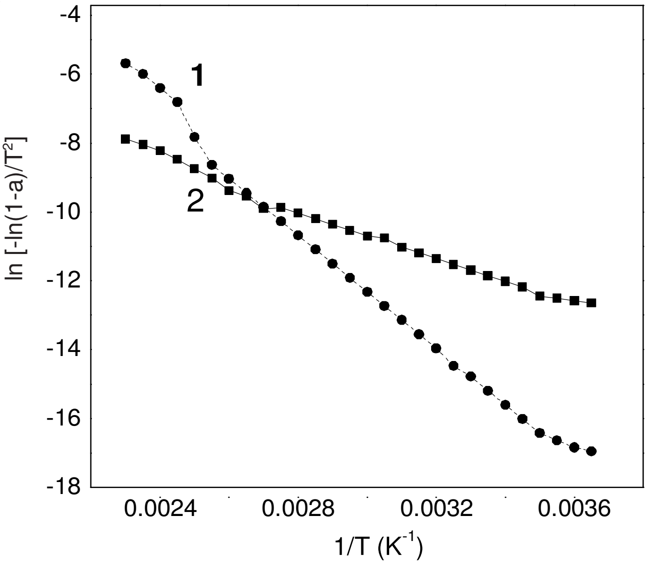

Fig. 2. TG dynamics curves of before (curve 2) and oxidization (curve 1) of lignite

TABLE-1
PYROLYSIS REACTION KINETICS PARAMETERS BEFORE AND AFTER LIGNITE OXIDATION

| Samples | Contrast | Activation Energy E (kJ/mol) | Frequency Factor A (1/s) | ΔE (kJ/mol) |
|---|---|---|---|---|
| HM | Original samples | 27.439 | $2.64 \times 10^{10}$ | 39.07 |
| | Oxidized samples | 66.510 | $3.02 \times 10^{10}$ | |

In comparison to thermal dynamic mechanism function of lignite shown in Fig. 2 before and after oxidization, the slope of oxidized coal samples was clearly larger than that of initial ones, indicating activation energy of coal samples after oxidization largened. It can be seen from Table-1, activation energy increased by 39.07 kJ/mol from 27.439 kJ/mol of original coal samples to 66.51 kJ/mol of oxidized ones. Activation energy of original lignite is so low that it needs less energy from initial state to activate one. Therefore, under the effect of oxidization on the original coal samples placed in the open air, original lignite samples release lots of caloric. With the discharge of liquid volatiles (mainly coal tar) and comprehensive pyrolysis of polycyclic aromatic hydrocarbons, the coal samples are extremely easy to catch fire, that is the temperature rise to ignition temperature. Reversely, activation energy of coal samples rises after oxidization, more energy were needed to get to activated state, leading to the release of less caloric.

## Conclusion

In summary, the following conclusions were obtained:

(1) Change of TGA and DSC curves at characteristic spot reflected physical adsorption, chemical adsorption and process of chemical reaction and molecular structural conversion in coal.

(2) In comparison to that of original lignite, the dynamics was discussed in different transformation ratio region, five stages of coal oxidation at low temperature was verified and mechanism function and thermal dynamic parameters of oxidization pyrolysis process of coal were worked out through Coats Redfern integral method.

(3) 27.439 kJ/mo of activation energy of original lignite samples was worked out by analysis of TG and DTG curves. The apparent energy needing to oxidize coal samples at low temperature was low, resulting in the easy oxidization of lignite. The activation energy of lignite increased by 39.07 kJ/mol influenced by spontaneous combustion oxidization in air, The more the energy needed to get activation state, the stronger the inertia of lignite caused by oxidization was.

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