Research article

The estimation of the kinetic parameters of low-temperature coal oxidation

Vladimir A. Kaminsky[1], Nina Yu. Obvintseva[2], and Svetlana A. Epshtein [1,]*

[1] Scientific-research testing laboratory "Physics and Chemistry of Coals", National University of Science and Technology "MISiS", 4 Leninsky prospekt, Moscow, 119049, Russian Federation

[2] Department of Physics, National University of Science and Technology "MISiS", 4 Leninsky prospekt, Moscow, 119049, Russian Federation

* Correspondence: Email: apshtein@yandex.ru; Tel: +7-499-237-29-59.

Abstract: Coals self-heating reasoned by their oxidation processes often could cause spontaneous combustion that may occur during all the stages of coal production, storage, transportation and utilization. The steady-state method enables determination of the critical ambient temperature, above which spontaneous combustion occurs, as a function of the reactor's size. These critical ambient temperatures are used to calculate the kinetic constants of oxidation coal. The transient method (or Chen method) is applied to directly estimate the rate of oxidation by determining the crossing point, when the thermal conduction term near the center of a cylinder becomes zero. A modified method is proposed for determining the kinetic constants of coal oxidation from the steady-state heating temperature at the center of the reactor. The method is based on the dependence of the dimensionless temperature on the Frank-Kamenetskii parameter. The kinetic constants have been calculated from the results of a numerical experiment with a cylindrical reactor.

1. Introduction

Coal oxidation at ambient temperatures is considered the main reason for products quality and energy losses. Chemisorption and oxidation occur when coal is exposed to air at relatively low

temperatures (below 100 ºC). Moreover, as such processes are exothermal, this may also lead to self-heating (accelerating the oxidation reaction) and spontaneous combustion events during production, storage, transportation and utilization of coal [1,2,3].

There exist a certain amount of instrumental methods and techniques for characterization of coals propensity to self-heating at oxidation. The most widely used one is the so-called R_{70} method [4,5]. The essence of this method is as follows. The grinded (with particle sizes of <212 μm) coal sample is dried in adiabatic oven at temperature of 105–110 ºC for 15 hours under inert gas flow, then cooled to 40 ºC in the same environment, and after that is being stored in the oxygen-rich air flow at the temperature of 40 ºC. Under the latter conditions, coal oxidation is being initiated and the processes of self-heating are observed. The average rate of the coal heating from 40 to 70 ºC is considered to be the index R_{70} (ºC/h). The higher the value of such index, the more prone the coal is to spontaneous combustion. Such method is the most efficient one with respect to simple characterization of coals propensity to oxidation and self-heating, but unfortunately there exist some disadvantages connected with the method of samples preparation, namely, their drying at high temperatures which may lead to irreversible alterations of coals properties.

Crossing Point Temperature (CPT) is another method widely applied for characterization of coals propensity to spontaneous combustion [6,7]. Here, the coal sample is placed in the oven which is being heated with constant rate. Within this method, a rate of coal sample heating is compared with the rate of the oven walls heating at the condition of constant air supply to the sample. In comparison with the aforementioned R_{70} method, CPT allows *in situ* coals samples testing, but still there are some disadvantages connected with the samples moisture, particles sizes, etc.

Other promising methods of characterization of coals spontaneous combustion due to oxidation are thermogravimetric analysis (TGA) [8] and differential scanning calorimetry [9]. Despite the fact that these approaches also allow studying of coal *in situ*, they also have disadvantages, namely, the oxidation effects are observed here at the temperatures much higher than ambient (over 200 ºC).

In order to completely describe the behavior of systems prone to spontaneous combustion, one should have sufficient information on the mechanism and kinetics of the characteristic chemical reactions considering also temperature and the conditions of heat loss to the surroundings. The activity of processes in the system depends on numerous factors, including the chemical composition, supramolecular structure, and porosity of the coal, as well as ambient conditions (air humidity, air flow, etc.). Many authors report experimental data on the effects of individual factors on the chemical activity of coal and use them as the basis for kinetic models of self-heating (e.g. see [1,2,10–13] for review). Although, it seems difficult to develop a complete kinetic model allowing the behavior of coal under real conditions to be predicted.

In order to simplify the description of the self-heating process, the interaction of coal with air is assumed to be a single exothermal reaction. The chemical activity of coal is estimated from apparent kinetic constants of the reaction, namely, the activation energy and the pre-exponential factor. They are commonly estimated using thermal methods [11–18] based on the results of direct laboratory measurements of thermal effects during oxidation. Kinetic constants evaluation within the thermal steady-state method is based on Frank-Kamenetskii (F-K) analysis [19] which was originally developed to determine the critical conditions of spontaneous combustion when the kinetics of the process is known. Thermal methods solve the inverse problem, i.e., determination of the kinetic constants when the parameters corresponding to the critical conditions of the system are known. This requires estimation of the relationship between the characteristic temperature and the critical F-K

parameter (δ_{cr}) determining the critical conditions under which a steady-state temperature profile in the system becomes impossible. The parameter δ_{cr} is preliminarily calculated for the laboratory reactor used in the study; the characteristic temperature is estimated from the results of a thermal experiment on coal heating in the reactor with the temperature on its surface maintained constant.

One of the most useful methods for evaluation of the relationship between δ_{cr} and the critical ambient temperature ($T_{s\,cr}$) (at which the temperature at the center of the sample drastically rises) is the traditional steady-state thermal method [3]. The kinetic constants are determined from the plot of

$\ln\left(\delta_{cr} T_{s\,cr}^2 / R^2\right)$ versus $1/T_{scr}$ (where R is the characteristic size of the reactor) based on experimental

data obtained for different sizes of laboratory reactors with the δ_{cr} parameter known for each of them. In thermal experiments, the crushed coal in a cylindrical laboratory reactor is placed into an oven where the constant temperature is maintained. The experiments are usually carried out at temperatures above 100 °C, because rapid heat loss to the surroundings of the sample makes it impossible to observe sample heating caused by the exothermal reaction at lower temperatures. It takes a series of thermal experiments to determine the critical temperature for each reactor.

In order to reduce the number of experiments, a transient method (the Chen method) has been proposed [17,18]. The estimation of the kinetic constants in this method is based on determining the rate of temperature change at the center of the reactor at the moment of time when the thermal conduction term of the equation of heat balance near the center becomes zero. The temperature corresponding to this moment is estimated experimentally from the condition of equality of the temperatures at the center and a point near it; it is termed the crossing point temperature. This method is described in detail as applied to cylindrical reactors in the study [17]. In this study, the estimation of the crossing point temperature was based on determining the moment when only the radial component of the thermal conduction term became zero. Strictly speaking, however, the moment when the sum of the radial and vertical components of the thermal conduction term is equal to zero should be used in the calculations. As further development of the Chen method, a procedure has been suggested for estimating the kinetic parameters from the dependence of the dimensionless crossing point temperature (θ_{cpt}) on the F-K parameter [19]. This dependence for an infinite slab has been shown to have the form $\theta_{cpt} = 0.1\delta$.

These transient methods for estimation of the kinetic parameters have allowed the number of experiments to be reduced compared to the steady-state method. The aim of the current work is to present a possibility of the same reduction in the context of the steady-state approach using experiments where critical conditions are not reached. To this end, a modified method for estimation of the kinetic parameters from the temperature at the center of a laboratory reactor in the steady-state mode is proposed. It was also established how the calculated values of the kinetic constants depend on whether or not the oxygen consumption in the oxidation reaction is taken into account.

2. Modified Steady-State Analysis

As noted above, the traditional steady-state approach to the estimation of the kinetic constants requires that the critical conditions characterized by the critical F-K parameter (δ_{cr}) be found. These conditions for each reactor are determined in a series of experiments at different temperatures on the sample surface. Let us consider how the results of a thermal experiment where the system goes to a steady state without reaching the critical conditions can be used for determining the kinetic constants.

It is suggested that the relationship between the F-K parameter and the dimensionless temperature (θ_c) is used in the steady-state mode at the center of the laboratory reactor, where heating is the most intense.

Coal heating is described by an unsteady-state energy balance equation for the case of an internal heat source:

$$\rho C_p \frac{\partial T}{\partial t} = k\Delta T + QW(T),$$ (1)

where T is the temperature (K), ρ is the bulk density of coal (kg m^{-3}), C_p specific heat capacity of coal (J kg^{-1} K^{-1}), k is the thermal conductivity of coal (W m^{-1} K^{-1}), Q is the heat of oxidation (J kg^{-1}) released as a result of the reaction. It is assumed that the reaction rate depends on temperature according to the Arrhenius law: $W(T) = A\exp(-E/R_gT)$, where A is the pre-exponential factor (s^{-1}) which includes the concentration of the reagents and E is the apparent activation energy (J mol^{-1}), R_g is the universal gas constant (8.314 J mol^{-1} K^{-1}). The consumption of the reagents in the course of oxidation is not taken into account, because this would substantially complicate the task. The use of Eq. (1) requires preliminary determination of parameters of the coal, including its density, thermal conductivity, and heat of reaction. In analyzing the results of thermal experiments, it is convenient to go from Eq. (1) to the equation describing the rate of temperature change:

$$\frac{\partial T}{\partial t} = a\Delta T + B\exp(-E/R_gT).$$ (2)

Here a is the temperature conductivity coefficient (m^2/s), $B = QA/(C_p\rho)$ is a parameter that includes the constant characterizing the reaction rate and the thermophysical constants of the system (Ks^{-1}); B determines the rate of temperature rise as a result of the exothermal oxidation reaction under adiabatic conditions. Equation (2) allows calculation of the kinetic parameters E and B provided that the coefficient a is known. The number of variables in Eq. (2) can be reduced using the F-K approximation to the Arrhenius term [19]. In order to obtain scaled dimensionless variables the dimensional variables are divided by their scales: length, $\xi = x/R$, where R is the characteristic size (the radius of the reactor); time, $\tau = at/R^2$; and temperature, $\theta = E(T - T_s)/R_gT_s^2$, where T_s is the temperature of the reactor walls. Equation (2) in dimensionless variables takes the form

$$\frac{\partial \theta}{\partial \tau} = \Delta_\xi\theta + \delta\exp(\theta).$$ (3)

Here, Δ_ξ is the Laplacian operator written in dimensionless variables and $\delta = \dfrac{E R^2 B}{R_g T_s^2 a}\exp(-\dfrac{E}{R_g T_s})$ is the dimensionless F-K parameter. The solutions of Eq. (3) are determined by the F-K parameter. The conditions of combustion are characterized by the critical value δ_{cr}. The condition $\delta = \delta_{cr}$ corresponds to the critical state where steady-state distribution becomes impossible. At $\delta < \delta_{cr}$, a steady-state temperature distribution is formed in the system; at $\delta > \delta_{cr}$, heat generation exceeds heat loss to the surroundings, which leads to self-heating of the system followed by spontaneous combustion. The parameter δ_{cr} is calculated for a given system with known thermophysical parameters and a prespecified geometry.

Following F-K method it is possible to obtain the correlation between δ parameter and a dimensionless temperature θ_c in a steady state inside the central point of the laboratory reactor. To do this it is suffice to solve the steady state temperature distribution problem taking into account the chemical reaction:

$$\Delta_\xi \theta = -\delta \, e^\theta . \tag{4}$$

The solution of the equation (4) corresponds to a steady state temperature distribution. Numerical solution of Eq. (4) has yielded the values of the dimensionless temperature at the center of the reactor (θ_c) at different values of δ for a cylindrical reactor with a height-to-diameter ratio of h/d = 1 (Table 1). The boundary condition at the sample surface is $\theta_c = 0$. It is convenient to represent the solution of this equation in a plot as the dependence $\delta = f(\theta_c)$ (Fig. 1, curve 1). It is possible to approximate this dependence with the function

$$\delta = 3.15(1 - \exp(-\theta/0.55)), \tag{5}$$

where $\delta = \dfrac{ER^2 B}{T_S^2 R_g a} \exp\left(-\dfrac{E}{T_S R_g}\right)$ and $\theta = \dfrac{E(T_C - T_S)}{T_S^2 R_g}$, T_c is the temperature at the center of the reactor in the steady-state mode, T_S is the temperature of the reactor walls. Figure 1 also shows the relation between dimensionless temperature (θ_c) and δ for cylindrical reactors with $h/d = 2$ and $h/d = 5$ (Fig. 1, curves 2 and 3, respectively). The parameters of the equation $\delta = f(\theta_C)$ have been found for $\delta < \delta_{cr}$, i.e., for the case where critical conditions have not been reached. The critical values of the F-K parameter for cylindrical reactors with finite length can be obtained by solving the equation (4) numerically. In the extreme case of $h \gg d$, the parameter δ_{cr} should approach the critical value for an infinite cylinder, $\delta_{cr} = 2$ [19].

Table 1. The values of the dimensionless temperature at the center of the reactor (θ_c) at different values of δ for a cylindrical reactor (h/d = 1).

δ	θ_C	δ	θ_C
0	0	2.1	0.664
0.25	0.052	2.2	0.7242
0.5	0.1082	2.3	0.792
0.75	0.1693	2.4	0.8704
1	0.2365	2.5	0.9644
1.25	0.3112	2.6	1.0842
1.5	0.3956	2.65	1.1617
1.75	0.4932	2.7	1.2615
2	0.6098	2.75	1.4143
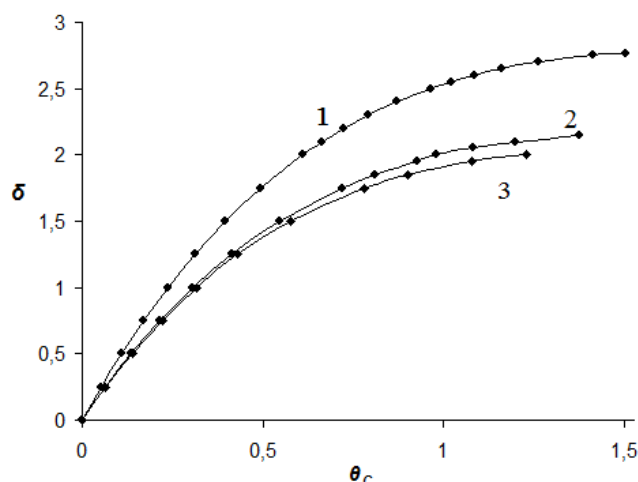
Figure 1. The dependences $\delta = f(\theta_C)$ **for reactors with *h/d* ratios of (1) 1, (2) 2, and (3) 5.**

The explicit form of the equation $F(\delta, \theta_c) = 0$ in the unknown parameters E and B is obtained by substituting the expressions for δ and θ into Eq. (5). The temperature at the center of the reactor (T_c) when the steady-state mode is established should be estimated from the results of a thermal experiment under the conditions of a constant temperature at the walls (T_s). The experiment should be performed several times at different T_s values. In this way, the pairs of temperatures (T_{s1}, T_{c1}), (T_{s2}, T_{c2}), etc. are determined. Each (T_s, T_c) pair should be substituted into the equation $F(\delta, \theta_c) = 0$. This yields a set of simultaneous algebraic equations whose solution allows the apparent kinetic constants to be determined.

3. Results and Discussion

### 3.1. An Example of Calculation of the Kinetic Parameters

Let us consider an example where the procedure described above is used to calculate the kinetic parameters E and B for a cylindrical reactor with $h/d = 1$. The values of the kinetic parameters can be determined from the results of two thermal experiments. The temperatures at the center of the reactor (T_{c1} and T_{c2}) in the steady-state mode can be estimated by numerically solving Eq. (1). The calculations have been performed for a cylindrical reactor with equal height and diameter of $h = d = 0.1$ m. In this study, the thermophysical parameters have been taken from [17]: $E = 101.7$ kJ/mol and

$B = 1.1 * 10^{11}$ K/s, $a = 1.5 \bullet 10^{-7}$ m^2/s. In our calculations, the temperature at the sample surface has

been taken to be $T_{s1} = 373.15$K (100 °C) in the first case and $T_{s2} = 383.15$K (110 °C) (in the second case); in the center, the symmetry condition has been assumed to be satisfied. The calculated temperatures at the center of the reactor are $T_{c1} = 376.05$K (102.9 °C) and $T_{c2} = 392.85$K (119.7 °C), respectively.

In order to determine the parameters E and B, let us rewrite Eq. (5) explicitly:

$$\frac{ER^2 B}{T_S^2 R_g\, a}\exp\left(-\frac{E}{T_S R_g}\right)=3.15\left(1-\exp\left(-\frac{E(T_C-T_S)}{0.55\cdot T_S^2 R_g}\right)\right),\qquad(6)$$

which allows us to substitute the temperatures $(T_{s1},\ T_{c1})$ and $(T_{s2},\ T_{c2})$. The result is a system of two equations with two unknowns, E and B. By dividing the first equation of the set of equations by the second we will get the equation in only one unknown E. It is convenient to solve this equation using a graphical calculation. Then we will evaluate the parameter B. The following kinetic parameters were obtained using this procedure for the aforementioned system of equations: E = 99.7 kJ/mol and

$B = 1*10^{11}$ K/s. The value of the activation energy obtained by solving the inverse problem differs

from that used in calculating the temperature by about 1%.

For a discriminating comparison between the temperatures used in Chen's method and in a proposed method we consider the temperature profiles in the reactor for the cases when the crossing point temperature occurs (Fig. 2, curve 1) and when the steady state is established (Fig. 2, curve 2) at 110 °C (T_s). As seen from Fig. 2, in an experiment where critical conditions are not reached, the crossing point temperature only slightly differs from the temperature at the reactor wall, which is inconvenient for analysis of the experimental data. The temperature at the center of the reactor in the steady-state mode is much higher; therefore, it is more suitable to use this value as a characteristic temperature.
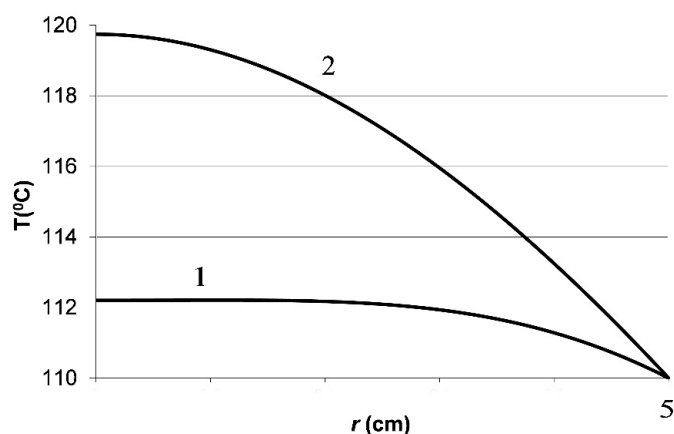
Figure 2. Temperature profiles in the reactors when (1) the crossing point temperature occurs and (2) the steady state is established (the temperature at the surface was 110 ºC).

In our modified method for estimating the kinetic constants of coal oxidation, the temperature in the steady-state mode, where the critical conditions are not reached, serves as a characteristic temperature. One should only experimentally measure the temperature at the center of the sample and know the temperature conductivity coefficient to determine the unknown parameters.

3.2. The Effect of Oxygen Consumption in Estimating the Kinetic Constants

The solution of the heat conductivity Eq. (1) yields the relationships from which the kinetic

constants can only be determined if the concentrations of the reagents are assumed to be constant. This limits the use of thermal methods based on the F-K analysis. To use this approximation, one should estimate the conditions of its applicability. For this purpose, let us recalculate the temperature in the sample during the heating, now with the oxygen consumption in the oxidation reaction taken into account. It is assumed that there is no forced convection, oxygen transport being accounted for by molecular diffusion.

Let us consider heating of coal in a cylindrical basket-type reactor, which ensures air supply to the coal. Numerical calculations will be performed for a system with the same parameters as in the system considered above, where the oxygen expenditure was not taken into consideration. It is assumed that, at the initial moment of time, oxygen is evenly distributed in the pores between granules throughout the rector. The coal in the reactor is considered as a quasi-homogeneous medium with an effective coefficient of diffusion. The initial oxygen concentration in the sample (C_0) is determined from the condition of equilibrium with the ambient air; the porosity factor is assumed to be 30%.

Within the quasi-homogeneous approximation, the process of heating is described by the equations of thermal conduction and diffusion containing a reaction term; the reaction is assumed to be of the first order with respect to oxygen:

$$\rho C_p \frac{\partial T}{\partial t} = k\nabla^2 T + QA\exp\left(-\frac{E}{R_g T}\right)\cdot\frac{C}{C_0},$$

$$\varepsilon\frac{\partial C}{\partial t} = D\nabla^2 C - A\exp\left(-\frac{E}{R_g T}\right)\cdot\frac{C}{C_0}. \tag{7}$$

Where C is the oxygen concentration (mol L^{-1}) (it is taken into consideration that the pre-exponential factor includes the concentration C_0); D is the diffusion coefficient in the porous medium, ε - porosity. The system of equations (7) was numerically solved under the boundary conditions of constant temperature T_s and oxygen concentration C_0. In the calculations, the kinetic parameters of the coal from the study [17] (see above) was used; it is suggested that they correspond to the characteristic of coal saturated with oxygen. The temperatures at the surface of the sample were specified as T_{s1} = 373.15 K (100 ºC) and T_{s2} = 383.15K (110 ºC).

The calculations have shown that, when the steady-state mode has been reached, the oxygen concentration in the center of the sample is decreased by about 4% in the first case and about 10% in the second case (Fig. 3, curve 1). This oxygen "deficit" leads to a decrease in temperature. In the steady-state mode, the temperature is settled at T_{c1} = 375.95K (102.8 ºC) and T_{c2} = 391.75 K (118.6 ºC) in the first and second cases, respectively (Fig. 3, curve 2). For comparison, the respective temperatures obtained for this system without oxygen consumption taken into account are 376.05K and 392.85K (see above).

Let us estimate how the decrease in the T_c–T_s value due to the decrease in oxygen concentration affects the values of the kinetic constants calculated by the modified method. For this purpose, let us use the temperatures (T_{s1}, T_{c1}) and (T_{s2}, T_{c2}) calculated with the oxygen consumption in the sample taken into account. The kinetic parameters determined by our method are E = 100 kJ/mol and B = 1.3·10^{11} K/s. This example shows that the consideration of the change in T_c due to oxygen consumption under the given conditions only slightly affects the values of the kinetic constants

calculated by the modified method. In the general case, a thermal experiment should be carried out under the conditions that ensure a negligibly small consumption of the reagents.
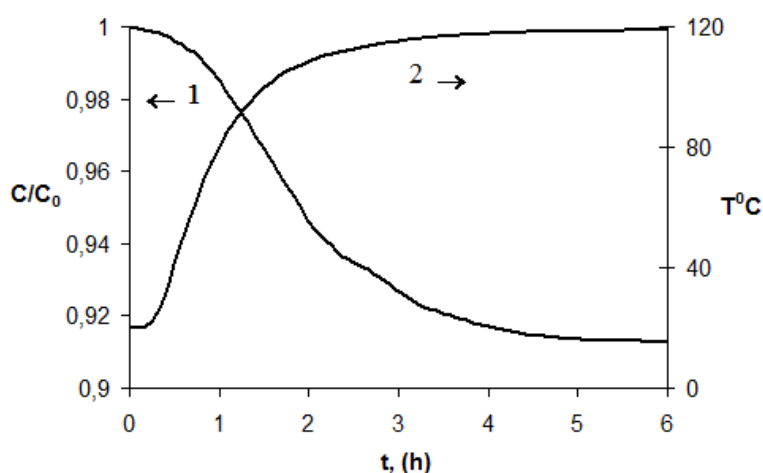
Figure 3. Changes in (1) the oxygen concentration and (2) the temperature at the center of the reactor with time (the temperature at the surface was 110 °C).

4. Conclusion

The modified method proposed here allows the kinetic constants of coal oxidation to be determined from the temperatures at the center and surface of the sample in a steady-state mode, where the critical conditions are not reached. The method is based on the dependence of the dimensionless temperature on the F-K parameter. This approach makes it possible to substantially reduce the number of experiments compared to the traditional steady-state method. The kinetic constants evaluation procedure was shown for the case of numerical experiment (as an example).

Acknowledgments

Conflict of Interest

All authors declare no conflicts of interest in this paper

References

1. Carras JN, Young BC (1994) Self-heating of coal and related materials: Models, application and test methods. *Prog Energ Combust* 1-15.

2. Wang H, Dlugogorski BZ, Kennedy EM (2003) Coal oxidation at low temperatures: Oxygen consumption, oxidation products, reaction mechanism and kinetic modelling. *Prog Energ Combust* 29: 487-513.
3. Bowes PC (1984) Self-heating: Evaluating and Controlling the Hazards. Amsterdam, The Netherlands: Elsevier Press.
4. Beamish BB, Barakat MA, George JDS (2000) Adiabatic testing procedures for determining the self-heating propensity of coal and sample ageing effects. *Thermochim Acta* 362: 79-87.
5. Qi X, Xin H, Wang D, et al. (2013) A rapid method for determining the R70 self-heating rate of coal. *Thermochim Acta* 571: 21-27.
6. Nugroho YS, McIntosh AC, Gibbs BM (1998) Using the crossing point method to assess the self-heating behavior of indonesian coals. *Symp (International) Combust* 27: 2981-2989.
7. Xuyao Q, Wang D, Milke JA, et al. (2011) Crossing point temperature of coal. *Min Sci Technol (China)* 21: 255-260.
8. Avila C, Wu T, Lester E (2014) Estimating the Spontaneous Combustion Potential of Coals Using Thermogravimetric Analysis. *Energ Fuel* 28: 1765-1773.
9. Li Z, Zhang Y, Jing X, et al. (2015) Insight into the intrinsic reaction of brown coal oxidation at low temperature: Differential scanning calorimetry study. *Fuel Process Technol* 147: 64-70.
10. Krishnaswamy S, Bhat S, Gunn RD, et al. (1996) Low-temperature oxidation of coal 1. A single-particle reaction-diffusion model. *Fuel* 75: 333-343.
11. Li B, Chen G, Zhang H, et al. (2014) Development of non-isothermal TGA–DSC for kinetics analysis of low temperature coal oxidation prior to ignition. *Fuel* 118: 385-391.
12. Chen G, Ma X, Lin M, et al. (2015) Study on thermochemical kinetic characteristics and interaction during low temperature oxidation of blended coals. *J Energ Inst* 88: 221-228.
13. Arisoy A, Beamish B (2015) Reaction kinetics of coal oxidation at low temperatures. *Fuel* 159: 412-417.
14. Nelson MI, Chen XD (2007) Survey of experimental work on the self-heating and spontaneous combustion of coal. Reviews in Engineering Geology: *Geol Soc Am* 31-83.
15. Parr SW, Coons CC (1925) Carbon Dioxide as an Index of the Critical Oxidation Temperature for Coal in Storage. *Ind Eng Chem* 17: 118-120.
16. Sujanti W, Zhang DK, Chen XD (1999) Low-temperature oxidation of coal studied using wire-mesh reactors with both steady-state and transient methods. *Combust Flame* 117: 646-651.
17. Chen X, Chong L (1995) Some Characteristics of Transient Self-Heating Inside an Exothermically Reactive Porous Solid Slab. *Process Saf Environ* 73: 101-107.
18. Chen X, Sidhu H, Nelson M (2013) A linear relationship between dimensionless crossing-point-temperature and Frank–Kamenetskii reactivity parameter in self-heating test at infinite Biot number for slab geometry. *Fire Safety J* 61: 138-143.
19. Frank-Kamenetskii DA (1969) Diffusion and heat transfer in chemical kinetics. New York: Plenum Press. p.370 p.