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ANALYSIS OF THE OXIDATION REACTIVITY OF CARBONACEOUS MATERIALS USING THERMOGRAVIMETRIC ANALYSIS

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The aim of this work is to develop a simplified, though rigorously based thermogravimetric analysis (TG) method to estimate intrinsic reactivity parameters (activation energy, *E*, and pre-exponential factor, *A*) for the oxidation in air of engineering carbonaceous materials. To achieve this aim, a modified Coats–Redfern method for analysing linear curves has been devised. The new method assumes first-order reaction kinetics with respect to carbon, and uses a statistical criterion to estimate an 'optimum' heating rate. For the oxidation in air of a model carbon, an optimum rate of 27 K min^{-1} was determined, at which E=125.8 kJ mol^{-1}. This is in good agreement with activation energies obtained using established, though more limited model-free or isoconversional methods.

Keywords: *carbonaceous materials, intrinsic reactivity, thermogravimetric analysis*

Introduction

Determining the intrinsic reactivity of carbonaceous materials is of considerable importance, especially in the coal industry, for example in combustion processes and steel-making. In particular, reactivity is used to compare different coals and coal blends, and is essential in the understanding of and predicting process performance. Reactivity, *k*, is generally defined in terms of the activation energy (E/kJ mol^{-1}) and a pre-exponential factor (A/s^{-1}) as an Arrhenius-type function:

$$k(T) = A\exp\left(-\frac{E}{RT}\right) \tag{1}$$

where T is the absolute temperature/K and R= =$8.314\cdot10^{-3}$ kJ K^{-1} mol^{-1} is the gas constant.

Thermogravimetric analysis (TG) has extensively been used in the assessment of *E* and *A* for carbons and other materials. Such techniques have been classified [1] as either model-fitting (i.e., identification of a kinetic reaction model) or isoconversional (i.e., model-free). Modern thermal analysis appears to prefer the use of the latter methods for two main reasons [1–4]: first, model-free kinetics are sufficiently flexible to allow for a change of mechanism during the course of the reaction; and second, mass transfer limitations are reduced by the use of multiple heating rates. By contrast, model-fitting kinetic methods generally involve a single heating rate, the disadvantage being that activation energy varies with heating rate due to mass/energy transfer effects [2, 5, 6].

In this work, an optimum heating rate for a model-fitting method is identified at which such effects appear to be minimised. At this heating rate, the activation energy is in a well-defined sense a 'true' value, i.e. not masked by mass/energy transfer limitations. This novel approach is further verified by conducting isoconversional analyses on the same material and comparing the activation energy values.

Experimental

Methods

The material used is a commercially available steam activated carbon (BPL) which is derived from bituminous coal and supplied by Calgon [7]. BPL has a BET surface area of ~1,000 m^2 g^{-1} (N_2 at 77 K) and a mean particle size of ~1 mm. This carbon was selected as a convenient homogeneous model for different coals. TG was carried out using a Setaram TG-92 thermogravimetric analyser. Oxidation of ~50 mg samples contained in alumina crucibles was carried out in flowing, dry air (16 mL [STP] min^{-1}), at the following heating rates 5, 10, 15, 20, 30 and 50 K min^{-1}, all from 293 to 873 K. This maximum temperature was selected to ensure that reaction took place within the chemical control regime for all the heating rates. This was established by preliminary runs showing that the conversion-time curve of BPL in air was independent of temperature below 873 K. Figure 1 is an example plot of original TG data (for a dry sample), plus the first derivative of these (referred to as DTG data), for a run at 5 K min^{-1}. The DTG data were calculated using a centred difference numerical differentiation formula. Note that, for clarity, the plot only includes

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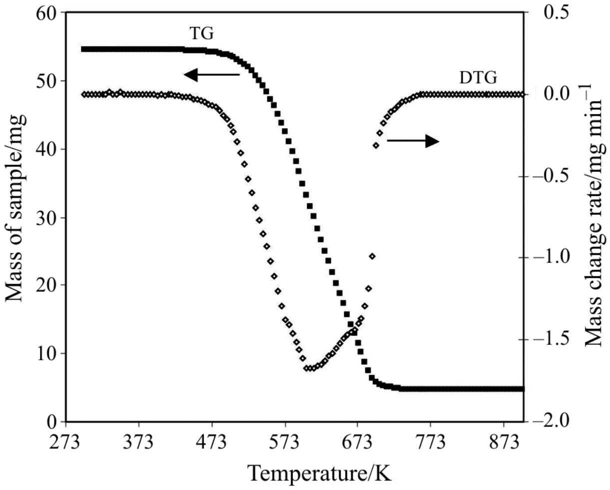

Fig. 1 ■ – Experimental TG and ◇ – DTG data for the oxidation of BPL carbon in flowing in air at 5 K min^{-1}

about 10% of the data (which are recorded every few seconds). Data such as those in Fig. 1, especially for low mass losses when it is assumed that the materials have not changed very much from their original states, are the subject of the analyses reported below. Selected runs were repeated two or three times and showed good repeatability. All mass change data are reported and analysed on a dry, ash-free (daf) basis (the ash content, ~10 mass%, having been determined previously by burning out samples in air).

Kinetic analysis

The oxidation of carbon in air is a thermal decomposition process, for which the kinetic equation can be expressed in differential form as

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=kg(\alpha) \qquad (2)$$

where $\alpha=[1-(m/m_0)]$ is the fractional mass conversion (m is daf sample mass and the subscript 0 refers to the initial mass) and t is time . The form of $g(\alpha)$ depends on the type of reaction model controlling the overall process. In the chemical control regime, carbon is generally agreed to react with oxygen following a single-step deceleration type function [8], in which case $g(\alpha)=(1-\alpha)$ (first-order kinetics with respect to carbon). Hence, for linear heating at rate $\beta=\mathrm{d}T/\mathrm{d}t$ Eq. (2) becomes

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T}=\frac{A(1-\alpha)}{\beta}\exp\left(-\frac{E}{RT}\right) \qquad (3)$$

Assuming that A and E are constants (which is appropriate for low conversions), this equation may be integrated with initial conditions T=0, α=0, to give

$$\ln(1-\alpha)=-\left(\frac{AR}{\beta E}\right)p(x) \qquad (4)$$

where $x=E/RT$ and

$$p(x)=\int_{x}^{\infty}\frac{\mathrm{e}^{-x}}{x^2}\approx\frac{\mathrm{e}^{-x}}{x^2}.$$

This approximation of $p(x)$ is given by Coats and Redfern [9] and applies for $2/x<<1$ (as for the analysis below). Equation (4) therefore reduces to

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right]=\ln\left(\frac{AR}{\beta E}\right)-\frac{E}{RT} \qquad (5)$$

Equation (5) is the model equation from which a straight line is obtained by plotting $\ln[-\ln(1-\alpha)/T^2]$ *vs.* $1/T$ at specific heating rate β; the activation energy is then obtained from the slope of this line, and the pre-exponential factor from the intercept. Note that while E appears in the intercept, this does not constrain the value of A estimated from the data.

For comparison with the proposed method, two well-known reaction model-free or isoconversional thermal analysis methods were also used. The first, due to Ozawa [10] and Flynn and Wall [11], is based on the following equation

$$\ln\beta=c+\left(1.052\frac{E}{RT_\alpha}\right) \qquad (6)$$

where c is a constant (not of any further significance in this analysis) and T_α is temperature at conversion α. Hence E is estimated from the slope of a plot of $\ln\beta$ *vs.* $1/T_\alpha$. The second method, due to Kissinger [12], is based on the following equation

$$\ln\left(\frac{\beta}{T_\mathrm{p}^2}\right)=d+\frac{E}{RT_\mathrm{p}} \qquad (7)$$

where d is a constant (not of any further significance in this analysis) and T_p is the temperature at the peak mass loss rate. Hence E is estimated from the slope of a plot of $\ln(\beta/T_\mathrm{p}^2)$ *vs.* $1/T_\mathrm{p}$. Note that while Kissinger's method was originally applied to DSC data [12], it is now also routinely applied to TG data [2, 13]. Although other more sophisticated model-free methods have recently been developed, both the Ozawa–Flynn–Wall and Kissinger methods are considered to be sufficiently accurate for comparison with the new method proposed here [4, 14].

Results and discussion

The model-fitting kinetic approach

Figure 2 comprises plots of original TG data for the oxidation of BPL carbon plus best fit curves for these using Eq. (5). Qualitatively the model appears to be a reasonable fit to the data at low conversion (where it is assumed that the material has not undergone much change from its original state, and therefore that both *E* and *A* are constants) for all heating rates used. Note that as in Fig. 1 only 10% or so of the data are plotted for the sake of clarity.

Table 1 lists best fit values of *E* and *A* estimated from the data using Eq. (5) for different heating rates. It appears that *E* and *A* decrease with increasing heating rate, as has been observed before [5, 6], and also that *E* and *A* are linearly correlated. The latter so-called compensation effect, which arises from the data and is not an artefact of the model, is currently the subject of further analysis by the authors.

In order to identify a value, or range of values, of the heating rate (and hence values of *E* and *A*) that gives the best overall fit to the data, the root mean

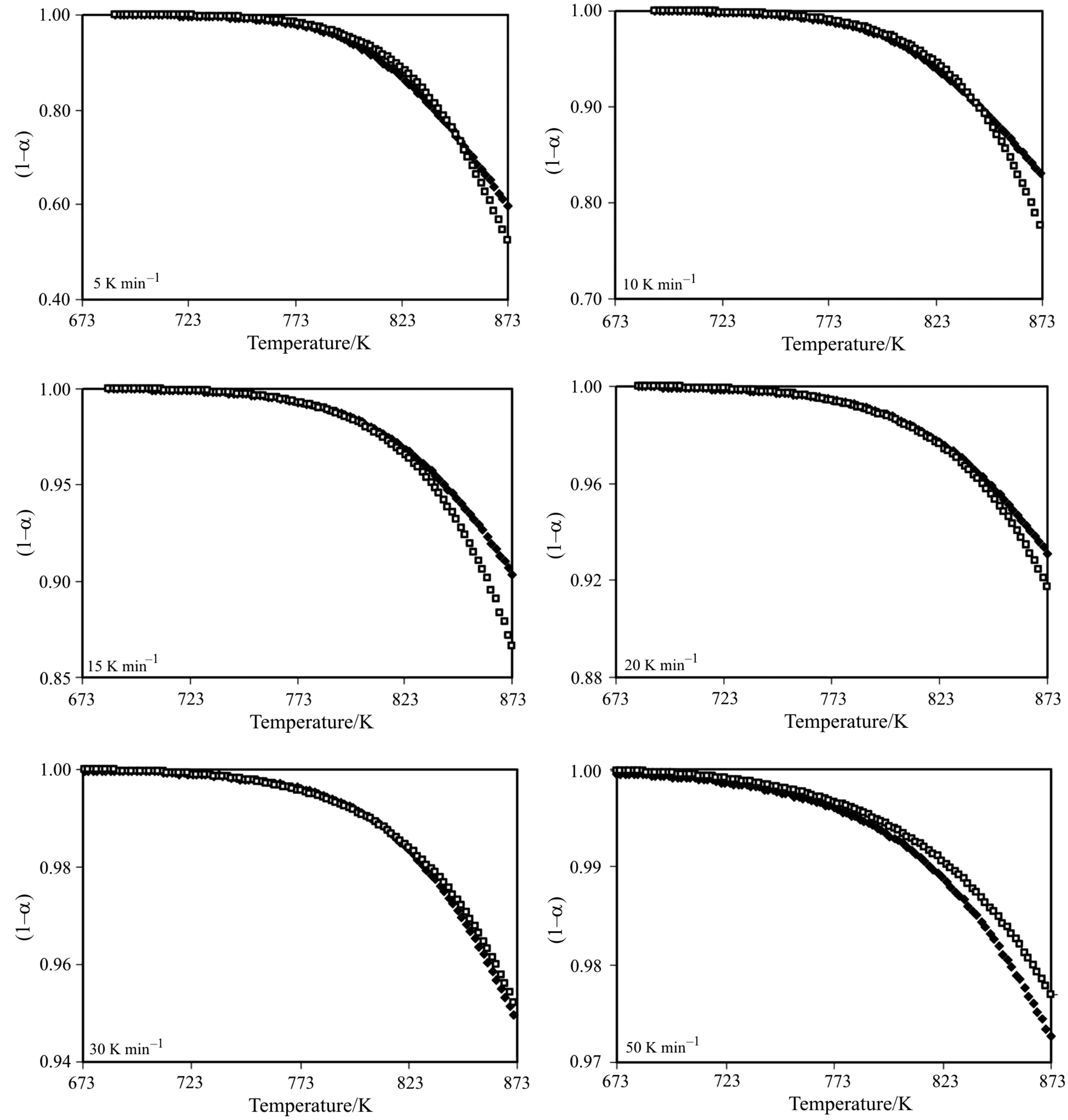

Fig. 2 Comparison of the □ – experimental conversion-temperature TG data ■ – with those predicted using best fit reactivity parameters for the different heating rates estimated using Eq. (5)

squared (RMS) error was determined for each TG curve as follows:

$$\sigma = \sqrt{\frac{\sum_{i=1}^{n} (\alpha_{i,calc} - \alpha_{i,exp})^2}{n}} \qquad (8)$$

where $\alpha_{i,calc}$ is the value of α calculated using Eq. (5) for the i^{th} data point (i=1, 2, 3,…, n), and $\alpha_{i,exp}$ is the experimental value of α. Figure 3 is a plot of (100×σ) (since σ is small) as a function of heating rate. This shows a broad minimum in the RMS error for heating rates in the range 25 to 35 K min^{-1}, with a probable minimum at 27 K min^{-1}, which corresponds to E=125.8 kJ mol^{-1} and ln(A/s^{-1})=9.5. These reactivity parameter values are considered to be optimum for the system being studied and the TG analysis method used, based on Eq. (5). They are also close to values reported in the literature for similar materials [15].

Results from model-free analysis methods

As previously mentioned, activation energy may be determined using model-free methods which do not assume any reaction mechanism. Figure 4 contains plots of TG data using both the Ozawa–Flynn–Wall and the Kissinger model-free methods, following Eqs (6) and (7), respectively. Note that only data for temperatures below 873 K are recorded in Fig. 4 to ensure chemical control oxidation. Both methods show linear behaviour, which indicates that they are good models for the selected TG data.

The activation energy estimated from Fig. 4a, for the Ozawa–Flynn–Wall method, is 136.5±±14.3 kJ mol^{-1}. This is for 3% conversion, which has the most data within the chemical control regime, and therefore provides the most accurate estimate of E. From the Kissinger method (Fig. 4b) only three heating rates have their peak temperatures, T_P, below 873 K and therefore in chemical control. The activation energy estimated using this method is 130.6±±11.0 kJ mol^{-1}. The values of E for both these model-free methods are close to that obtained using the modified Coats–Redfern approach, Eq. (5), though errors on the estimates are about an order of magnitude higher (Table 1). A further advantage is that the Coats–Redfern analysis also provides estimates of the pre-exponential factor, A, which are not available directly using the model-free methods.

Table 1 Best fit reactivity parameters (± one standard error) for the air oxidation of BPL carbon estimated using the modified Coats–Redfern model-fitting kinetic, Eq. (5)

Heating rate β/K min^{-1}	Activation energy E/kJ mol^{-1}	Pre-exponential factor ln$A$/s^{-1}
5	190.6±1.3	19.96±0.02
10	171.8±1.3	16.96±0.02
15	155.6±1.0	14.30±0.03
20	135.9±0.8	11.26±0.05
30	122.8±1.0	9.30±0.4
50	92.6±0.6	4.75±0.02

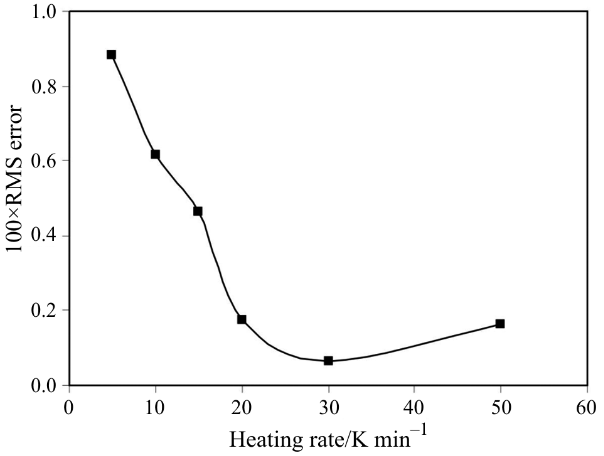

Fig. 3 (100×root mean squared error, σ) for the curve data as a function of heating rate, using Eq. (5) as a model. The curve through the points is a cubic spline interpolation

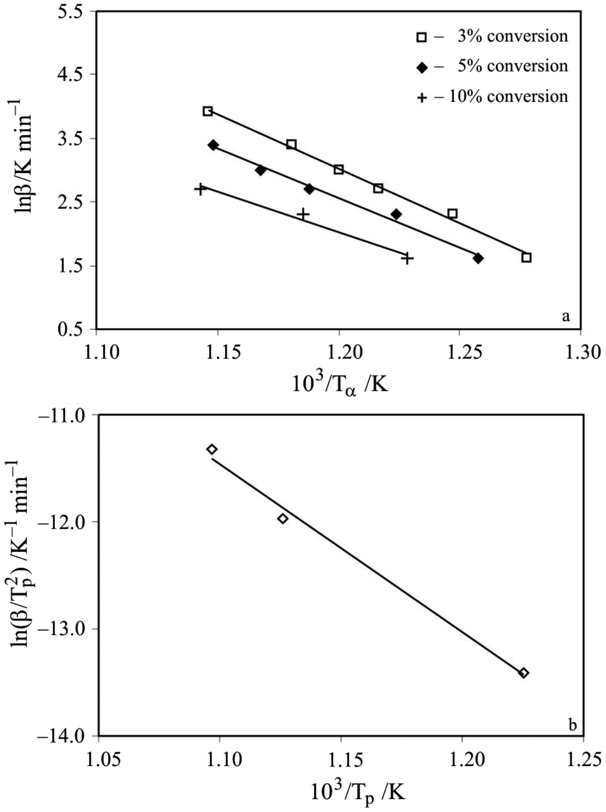

Fig. 4 Determination of activation energy by model-free methods: a – Ozawa–Flynn–Wall, Eq. (6); b – Kissinger, Eq. (7)

Conclusions

It has been shown that it is possible to identify a heating rate for non-isothermal TG that allows optimal estimates of the activation energy, *E*, and pre-exponential factor, *A*, to be made for the oxidation in air of a carbonaceous material in the chemical control regime. The activation energy obtained by this method (~125.8 kJ mol^{-1}) is in good agreement with values obtained using model-free (or isoconversional) methods and those reported in the literature for similar materials [14]. An advantage of the new method is that errors on estimates of *E* using it are about an order of magnitude lower than those obtained from the model-free methods. The new method also provides estimates of *A* which are not directly provided by the model-free methods. However, it is not clear how the heating rate to yield optimum estimates of reactivity parameters using the new method depends on the TG equipment used, the materials being studied and environmental conditions. It is conceivable that once an optimum heating rate is identified, it is applicable to any TG equipment, material or set of environmental conditions. In that case, it might only be necessary to carry out a few initial non-isothermal runs using the new method, rather than the multiple runs required for the model-free methods. This aspect is currently being investigated by the authors.

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References

1 M. E. Brown, Introduction to thermal analysis: techniques and applications. 2nd Ed. Kluwer Academic, London 2001.
2 T. Hatakeyama and L. Zhenhai, Handbook of thermal analysis, Wiley & Sons, Chichester 1998.
3 S. Vyazovkin, J. Therm. Anal. Cal., 64 (2001) 829.
4 S. Vyazovkin and D. Dollimore, J. Chem. Inf. Comput. Sci., 36 (1996) 42.
5 J. Zsakó, E. Kékedy and Cs. Várhelyi, Kinetic analysis of thermogravimetric data IV: influence of heating rate and sample mass on thermal decomposition. Thermal Analysis, Vol. 2. Davos: Proceedings 3rd ICTAC. 1971.W.M.
6 Wendlandt, Chemical analysis, Interscience Publishers, Vol. 10, 1964.
7 Calgon Carbon Corporation, Product bulletin: BPL 4×10 granular activated carbon, Pittsburgh 1998; LC – 103-08/98.
8 D. W. Van Krevelen, Coal: Typology-Chemistry-Physics-Constitution. 3rd Ed. Elsevier, Amsterdam 1993.
9 A. W. Coats and J. P. Redfern, Nature, 201 (1964) 68.
10 T. A. Ozawa, Bull. Chem. Soc. Jpn., 38 (1965) 1881.
11 J. H. Flynn and L. A. Wall, J. Res. Nat. Bur. Standards, 70A (1966) 487.
12 H. E. Kissinger, Anal. Chem., 29 (1957) 1702.
13 H. F. Mothé Filho, M. L. A. Gonçalves and C. G. Mothé, J. Therm. Anal. Cal., 67 (2002) 381.
14 M. J. Starink, Thermochim. Acta, 404 (2003) 163.
15 N. V. Russell, T. J. Beeley, C. K. Man, J. R. Gibbins and J. Williamson, Fuel Proc. Technol., 57 (1998) 113.