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A direct search method for determination of DAEM kinetic parameters from nonisothermal TGA data (note)

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Abstract

In this study, a simple direct search method to be used for the determination of distributed activation energy model (DAEM) kinetic parameters from the nonisothermal thermogravimetric analysis (TGA) data of coals has been introduced. Process steps of direct search method that depends on the grid technique have been given. The method has been applied to the nonisothermal TGA data of one Turkish coal and one imported coal, and DAEM kinetic parameters of these coal samples have been determined. Calculated model results from determined kinetic parameters have been compared with nonisothermal TGA data of the coals. © 2002 Elsevier Science Inc. All rights reserved.

Keywords: Distributed activation energy model (DAEM); Thermogravimetric analysis data (TGA); Direct search technique; Curve fitting

1. Introduction

In the coals containing a high proportion of volatile matter, a significant part of specific energy of the coal reaching to about 50% occurs as a result of combustion of volatiles [1–3]. The concept of devolatilization expresses the escape of the volatile matter because of thermal decomposition. Devolatilization takes place under either inert or oxidizing or reducing atmospheres;

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gasification, liquefaction, production of metallurgical coke and direct combustion are examples of such processes. Thermal decomposition mechanism must be known so that the design and control of these processes can be carried out.

The models explaining thermal decomposition of coal may be investigated under two main headings as single-reaction and multi-reaction models. The advantages, disadvantages, assumptions and restrictions of these models are given in the literature [1,3–6]. Distributed activation energy model (DAEM) is one of the multi-reaction models used widely to clarify the thermal decomposition of coal.

Determination of DAEM kinetic parameters has some mathematical difficulties. Structure of DAEM equation causes many difficulties in the using of general purpose curve fitting softwares. Hence many researchers who study on the subject develop own softwares. In this study, a direct search method to be used for the determination of DAEM kinetic parameters from the nonisothermal thermogravimetric analysis (TGA) data of coals has been presented.

2. Theory and method

2.1. DAEM equation

Assumptions and restrictions of DAEM, and the derivation of its equations can be found in the literature [6,7]. DAEM equation for the nonisothermal processes is given below:

$$1-x=\int_0^{\infty}\exp\left(-\int_0^{t}k_0\exp(-E/RT)\,\mathrm{d}t\right)\frac{1}{\sigma\sqrt{2\pi}}\times\exp(-(E-E_0)^2/(2\sigma^2))\,\mathrm{d}E. \tag{1}$$

In the above equation, E is the activation energy, E_0 the mean of activation energy distribution, k_0 the frequency factor, R the universal gas constant, T the absolute temperature, t the time, σ the standard deviation of the activation energy distribution and x the mass fraction of releasing volatiles.

2.2. Numerical solution of DAEM equation

When the numerical value of the frequency factor is assumed to be constant at 1.67×10^{13} 1/s [6], DAEM equation can be solved by using the numerical techniques for certain E_0 and σ values. A computer program which employs Simpson's 1/3 rule for integration has been developed by Güneş and Güneş [8] for the numerical solution of DAEM equation. In this study, this computer program will be used for the numerical solution of Eq. (1) and will be called as SOLVE-DAEM in Fig. 2.

In the numerical integration, first of all, the relation between temperature and time needs to be known. TGA is one of the most widely used thermoanalytical techniques to determine the weight loss of a sample as a function of time and temperature [9]. It can be performed either in the isothermal or nonisothermal mode. The nonisothermal mode has the advantage of requiring less experimental data than the isothermal mode [10,11]. In the nonisothermal TGA, the sample is heated by using a linear heating rate and change of the weight loss as a function of temperature or time is obtained:

$$T = a + bt. \tag{2}$$

In the above equation, T is the absolute temperature, a the initial temperature, b the heating rate and t the time. Nonisothermal TGA data of the investigated coals has been obtained at the heating rate of 20°/min. Therefore, $T = 293 + 20t$ equation will be used in numerical examples. In the previous study [12], the influences of various parameters on the numerical solution of Eq. (1) have been investigated. Therefore in the numerical integration of Eq. (1), 500 kJ/mol value can be used for the upper limit of dE integral. This value is so close to $E_0 + 3\sigma$ value where confidence interval of Gauss distribution is 99% [13]. Integral interval number of dE integral is better to be chosen as 50 both to have no oscillations in the results and to keep the solution time short. As the upper limit in the inner dt integral, the t value the solution of which is made at that moment is used. Integration step size was automatically adjusted by the program as numerical integration progressed.

The read values at certain t times from TGA curve are written in their parts in the following equation:

$$x = (w_0 - w_t)/(w_0 - w_f) \tag{3}$$

and the releasing volatile matter proportion is determined. In Eq. (3), w_0 is the initial weight, w_f the final weight and w_t the weight at time t of the sample analyzed by nonisothermal TGA.

2.3. Determination of DAEM parameters

If the frequency factor is assumed as constant, kinetic parameters of DAEM equation are E_0 and σ values. In the previous studies, these parameters were established using methods such as (i) nonlinear Hooke and Jeeves optimizing method [10]; (ii) Marquardt nonlinear regression method [14,15]. Structure of DAEM equation causes many difficulties in the using of general purpose curve fitting softwares. Hence many researchers who study on the subject develop own softwares. In this study a computer program based on direct search technique will be used. This technique involves solution of Eq. (1) repeatedly

for several values of E_0 and σ in order to determine these values which minimize the objective function

$$h2 = \sum_{j=1}^{n} (x_{j,\mathrm{TGA}} - x_{j,\mathrm{DAEM}})^2, \tag{4}$$

where $x_{j,\mathrm{TGA}}$ and $x_{j,\mathrm{DAEM}}$ are experimental and calculated values of mass fraction, respectively. n is data number.

E_0 values published in literature [2,4,6] are between 150 and 300 kJ/mol. Obtained values for σ are between 10 and 70 kJ/mol. If Eq. (1) is solved using certain E_0 and σ values between these limits, $x_{j,\mathrm{DAEM}}$ are obtained. If $x_{j,\mathrm{DAEM}}$ value is written together with TGA data of the sample ($x_{j,\mathrm{TGA}}$) in Eq. (4), a curve set similar to the one in Fig. 1 is obtained. Kinetic parameters searched for the coal studied on will be about E_0 and σ values where $h2$ has minimum value in these curves.

In order to determine the E_0 and σ values minimizing $h2$ value, a computer program performing direct search process with grid technique has been developed. The block diagram of this computer program is given in Fig. 2.

3. Results

For numerical examples, nonisothermal TGA data of one Turkish and one imported coal is used. Proximate and ultimate analyses of the coals are given in

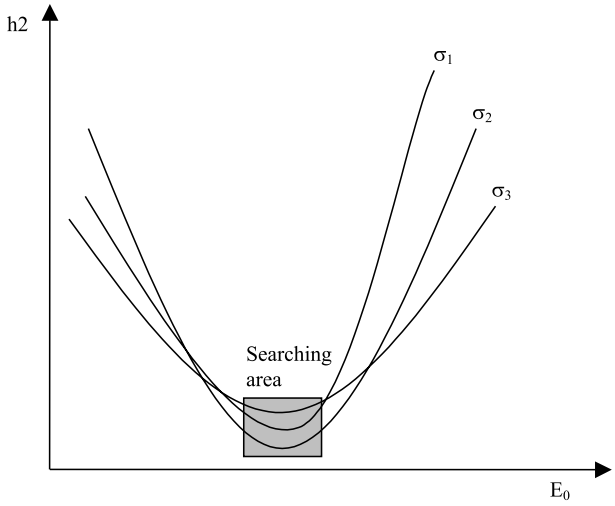

Fig. 1. The probable change of $h2$ depending on different E_0 and σ values.

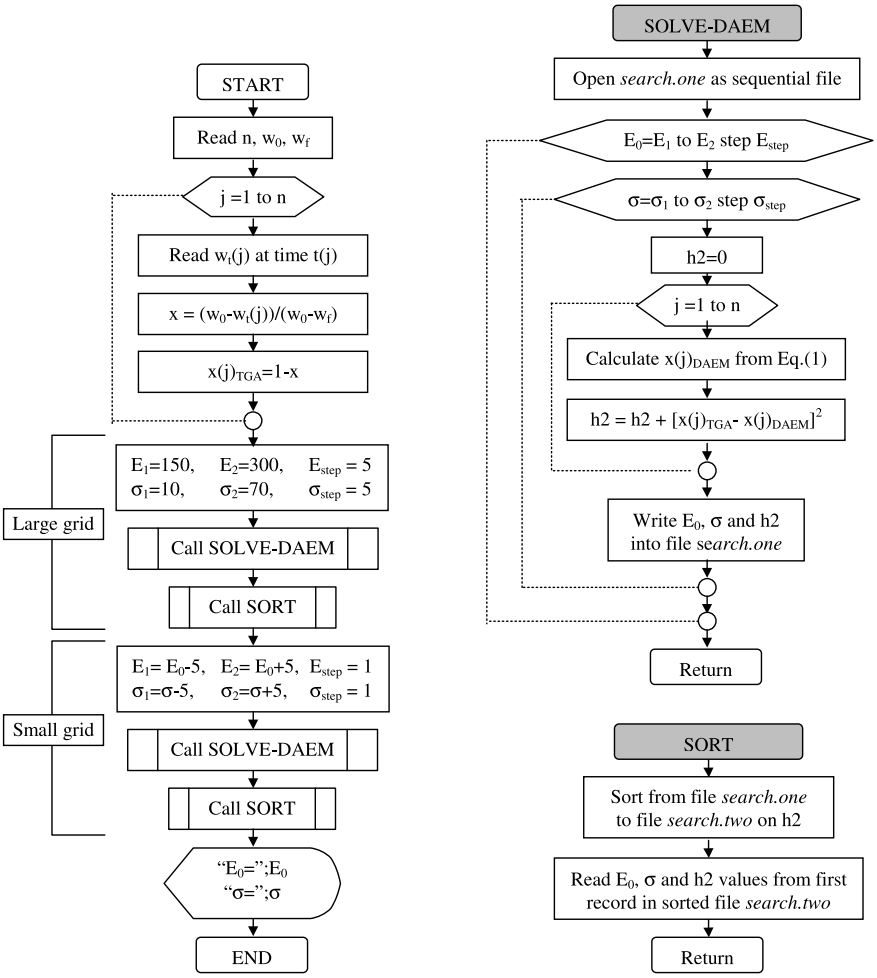

Fig. 2. The block diagram of computer program determining the E_0 and σ values from nonisothermal TGA data.

Table 1. Nonisothermal TGA data of coal samples have been obtained with a heating rate of 20°/min and a nitrogen flow rate of 250 cm^3/min.

The change of $h2$ values calculated at the end of large grid procedure for very high grid values ($E_0 = 150$–300 step 50 kJ/mol; $\sigma = 10$–70 step 30 kJ/mol) is given in Fig. 3. As seen clearly in this figure, large grid process must be applied to values proximate to E_0 and σ where $h2$ value shows minimum level. At the end of large grid procedure for $E_{step} = 5$ kJ/mol and $\sigma_{step} = 5$ kJ/mol

Table 1
Analyses of the coal samples

	Turkish coal	Imported coal
Proximate analysis (*wt%, as received*)		
Moisture	5.5	7.1
Volatile matter	35.0	42.8
Fixed carbon	49.8	42.7
Ash	9.7	7.4
Ultimate analysis (*wt%, db*)		
Carbon	69.1	65.3
Hydrogen	5.1	5.4
Nitrogen	1.7	1.6
Sulphur	1.3	0.3
Oxygen (by difference)	12.5	19.5

Table 2
Information in the first three records of *search.two* file sorted according to the $h2$ values at the end of large grid procedure

Turkish coal			Imported coal		
E_0 (kJ/mol)	σ (kJ/mol)	$h2$ $(\text{kJ/mol})^2$	E_0 (kJ/mol)	σ (kJ/mol)	$h2$ $(\text{kJ/mol})^2$
240	40	0.01768	225	30	0.03348
240	45	0.01882	220	30	0.03573
245	40	0.01947	220	25	0.03585

Table 3
Values used in small grid procedure

	E_0 (kJ/mol)			σ (kJ/mol)		
	Initial value	Final value	Step	Initial value	Final value	Step
Turkish coal	235	245	1	35	45	1
Imported coal	220	230	1	25	35	1

values, the first three records of *search.two* file sorted according to $h2$ values are summarized in Table 2. The initial, final and step values of E_0 and σ parameters that must be used in small grid process are given in Table 3 with the help of information given in the first line in Table 2. The kinetic parameters determined for the coal samples as a result of this search are presented in Table 4

Table 4
DAEM kinetic parameters for the coal samples

	E_0 (kJ/mol)	σ (kJ/mol)	$h2$ (kJ/mol)^2
Turkish coal	242	41	0.01633
Imported coal	223	29	0.03217

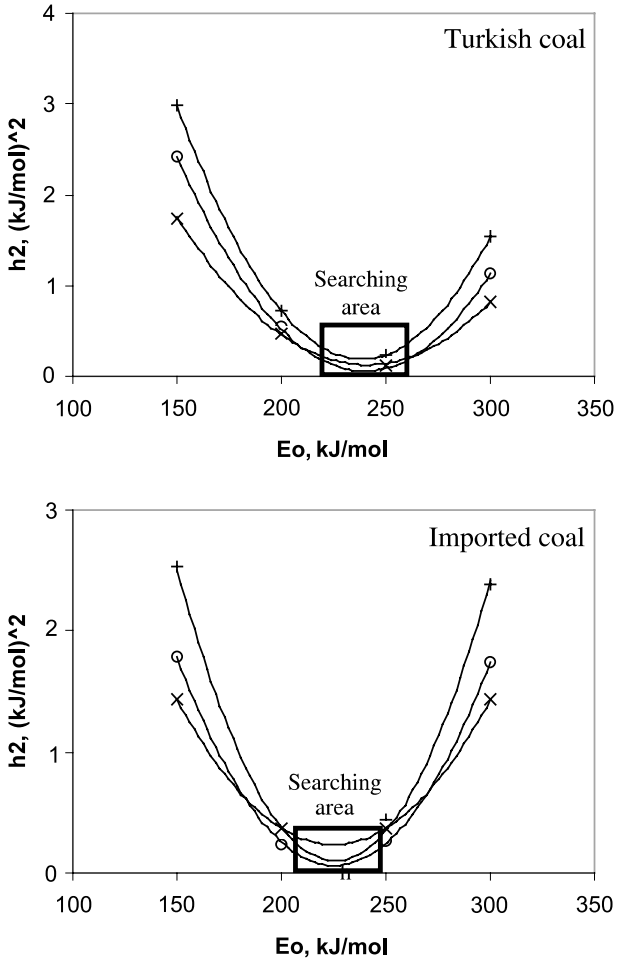

Fig. 3. The change of $h2$ values at the end of large grid procedure for $E_{step} = 50$ kJ/mol and $\sigma_{step} = 30$ kJ/mol. σ (kJ/mol): $+ = 10$, $o = 40$, $x = 70$.

and calculated weight loss curves are compared with nonisothermal TGA data in Fig. 4.

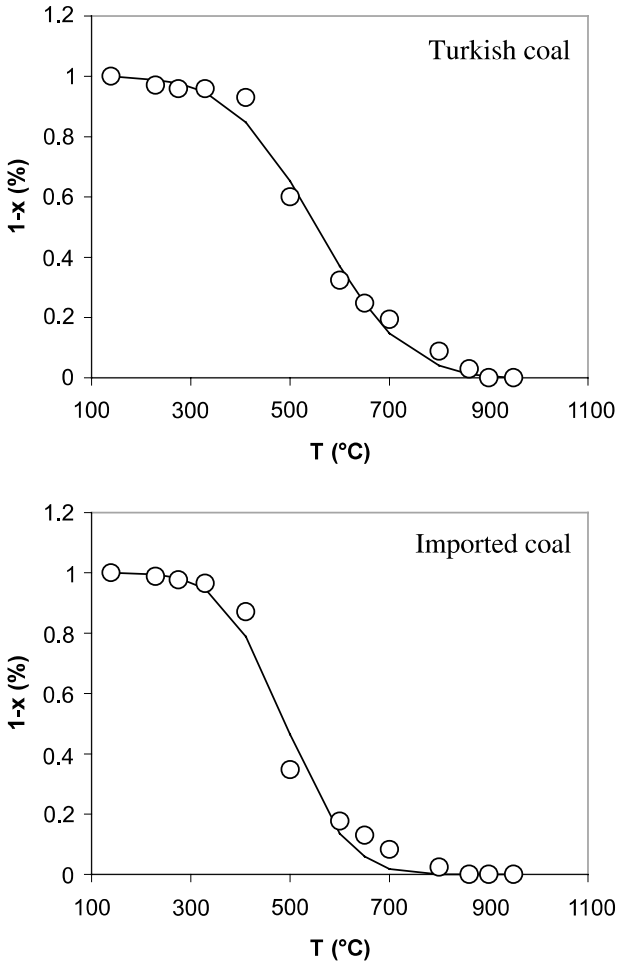

Fig. 4. Comparison of weight loss curves calculated from the distributed activation energy model with nonisothermal TGA data (○: TGA, ——: DAEM).

4. Conclusion

DAEM kinetic parameters used in the explanation of thermal decomposition processes can be determined easily from nonisothermal TGA data of sample and through a direct search method based on the grid technique presented in this study. Determined kinetic parameters can be used for design and control of thermal decomposition processes.

In the former studies [12,16–18], the frequency factor is also assumed as the one of the kinetic parameters of DAEM equation. The computer program presented in this study can be adapted according to this assumption.

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