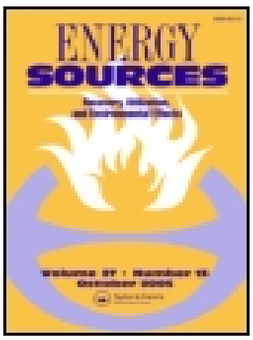

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Distributed Activation Energy Model Parameters of Some Turkish Coals

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Abstract *A multi-reaction model based on distributed activation energy has been applied to some Turkish coals. The kinetic parameters of distributed activation energy model were calculated via computer program developed for this purpose. It was observed that the values of mean of activation energy distribution vary between 218 and 248 kJ/mol, and the values of standard deviation of activation energy distribution vary between 32 and 70 kJ/mol. The correlations between kinetic parameters of the distributed activation energy model and certain properties of coal have been investigated.*

Keywords distributed activation energy model (DAEM), TGA, thermal decomposition kinetics

1. Introduction

A distinctive characteristic of Turkish coals is their relatively high (up to 40%) volatile matter (VM) content. Hence, understanding the behavior of VM is of paramount importance for technological applications and substantial effort has been devoted to study the devolatilization of Turkish coals (Urkan et al., 1987; Bilge, 1988; Ekinci et al., 1988; Urkan, 1990; Kucukbayrak, 1993; Urkan and Arikol, 1994; Gunes, 1997; Ceylan et al., 1999; Ballice, 2002; Ballice and Saglam, 2003; Kok, 2003; Guruz et al., 2004; Sinag, 2004). The concept of devolatilization expresses the releasing of VM because of thermal decomposition. Thermal decomposition models can be investigated under two main headings as single-reaction and multi-reaction models. The advantages, disadvantages, assumptions, and restrictions of these models are available in the literature (Pitt, 1962; Anthony and Howard, 1976; Suuberg et al., 1978; Brown, 1988; Saxena, 1990; Solomon et al., 1992; Brown et al., 2000; Maciejewski, 2000; Vyazovkin, 2000; Burnham, 2000; Roduit, 2000).

The Distributed Activation Energy Model (DAEM), representing multi-reaction models, is widely used for the pyrolysis of a range of materials, including coal, biomass, residual oils, and kerogen. In studies between 1980 and 1996, Turkish researchers were widely using the single-reaction models in the explanation of the thermal decomposition process (Gunes, 1997). The single-reaction models were also preferred by recent studies (Ceylan and Olcay, 1998; Kucukbayrak et al., 2001; Guldogan et al., 2000, 2001a, 2001b,

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2002; Kok, 2003; Guruz et al., 2004; Kizgut and Yilmaz, 2004; Sinag, 2004; Degirmenci and Durusoy, 2005; Duz et al., 2005).

In the other study (Gunes and Gunes, 2005), the single first-order reaction model was applied to the TGA data of 12 Turkish coals, and the single first-order reaction model kinetic parameters were determined. The purpose of this study is to apply the DAEM to non-isothermal thermogravimetric analysis (TGA) data of some Turkish coals.

2. Theory and Data

2.1. DAEM Equation

The DAEM treats the overall pyrolysis as a large number of independent, parallel first-order processes. This model assumes that the thermal decomposition of numerous components is described by a distribution of activation energies. Assumptions and restrictions of DAEM and the derivation of its equations can be found in the literature (Pitt, 1962; Anthony and Howard, 1976). The DAEM equation for the non-isothermal processes is given below:

$$1-x = \int_0^\infty \exp\left(-\int_0^t k_0 \exp(-E/RT)dt\right) \frac{1}{\sigma\sqrt{2\pi}} \exp(-(E-E_0)^2/(2\sigma^2))dE, \quad (1)$$

where E is the activation energy, E_o is the mean of activation energy distribution, k_o is the frequency factor, R is the universal gas constant, T is the absolute temperature, t is the time, x is the mass fraction of releasing volatiles, and σ is the standard deviation of the activation energy distribution.

2.2. TGA Data

In Eq. (1), the relationship between t, T, and x is determined by TGA. The 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 (Brown, 1988). It can be performed either in the isothermal or non-isothermal mode. The non-isothermal mode has the advantage of requiring less experimental data than the isothermal mode (Lee and Beck, 1984; Tia et al., 1991). In the non-isothermal 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:

$$T = a + bt, \quad (2)$$

where T is the absolute temperature, a is the initial temperature, b is the heating rate, and t is the time.

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

$$x = (w_i - w_t)/(w_i - w_f), \quad (3)$$

and the releasing VM proportion is determined. In Eq. (3), w_i is the initial weight, w_f is the final weight, and w_t is the weight at time t of the sample analyzed by non-isothermal TGA (Brown, 1988).

Proximate and ultimate analyses of the studied Turkish coals are given in Table 1. Non-isothermal TGA data of the coals have been obtained with a heating rate of 20 K/min and a nitrogen flow rate of 250 cm^3/min. The temperature interval of TGA data is between 140°C and 900°C.

Table 1
Proximate and ultimate analyses for 12 Turkish coals

Coal	Proximate analysis (wt% as-received)				Ultimate analysis (wt% db)			
	M	A	VM	FC	C	H	N	S
Amasra	5.5	9.7	35.0	49.8	69.1	5.1	1.7	1.3
Can	17.9	8.1	35.4	38.6	59.5	4.8	1.3	6.1
Esme	5.2	32.0	35.5	27.3	45.5	4.3	0.9	12.1
Gediz	1.6	15.7	35.8	46.9	64.1	4.8	0.8	7.7
Ilgin	13.5	11.2	43.0	32.3	55.0	4.9	0.8	2.4
Karliova	9.8	16.5	34.9	38.8	59.6	5.0	1.7	1.3
Kemerburgaz	34.3	11.5	32.7	21.5	51.1	4.9	0.8	3.6
Orhaneli	25.7	21.8	30.0	22.5	44.9	4.4	0.8	3.4
Seyitomer	23.7	10.0	36.9	29.4	55.2	5.2	1.2	1.1
Soma1	15.0	20.4	43.4	21.2	48.1	4.9	1.2	4.1
Soma2	15.6	10.1	36.8	37.5	64.5	5.0	1.3	0.6
Yatagan	30.7	12.8	36.0	20.5	49.0	4.8	0.7	3.9

3. Results and Discussion

When the numerical value of the frequency factor is assumed to be constant at 1.67E13 1/s (Anthony and Howard, 1976), the kinetic parameters of DAEM equation are E_o and σ values. In the previous studies, these parameters were established using methods such as:

1. Marquardt nonlinear regression method (Ciuryla et al., 1979; Thakur and Nuttall, 1987),
2. Nonlinear Hooke and Jeeves optimizing method (Tia et al., 1991),
3. Direct search technique (Gunes and Gunes, 2002).

In this study, the direct search technique was employed. This technique involves solution of Eq. (1) repeatedly for several values of E_o and σ in order to determine those values that minimize the objective function

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

where $x_{j,\mathrm{DAEM}}$ and $x_{j,\mathrm{TGA}}$ are calculated and experimental values of mass fraction, respectively. Since the TGA analysis of the coals were obtained with a heating rate of 20 K/min, $T = 293 + 20t$ equation was used in the numerical solution of DAEM equation. To obtain the $x_{j,\mathrm{TGA}}$ values, the mass fractions of volatiles releasing were calculated via Eq. (3) from experimental data of each coal. The block diagram of computer program determining the E_o and σ values from non-isothermal TGA data can be found in the other study (Gunes and Gunes, 2002).

The DAEM kinetic parameters determined for Turkish coals as a result of the direct search procedure are presented in Table 2, and calculated weight loss curves are compared

Table 2
Kinetic parameters of the distributed activation energy model for 12 Turkish coals

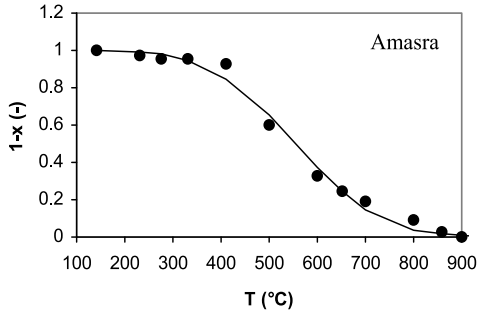
Coal	E_o, kJ/mol	σ, kJ/mol	h2, –	R2[a], –
Amasra	242	41	0.01633	0.99635
Can	240	58	0.00787	0.99792
Esme	228	32	0.02958	0.99395
Gediz	225	35	0.03673	0.99274
Ilgin	223	46	0.01132	0.99733
Karliova	238	34	0.01117	0.99777
Kemerburgaz	248	70	0.02606	0.99194
Orhaneli	242	66	0.01360	0.99599
Seyitomer	226	60	0.00972	0.99721
Soma1	218	49	0.01082	0.99734
Soma2	235	52	0.00895	0.99764
Yatagan	221	50	0.01232	0.99687

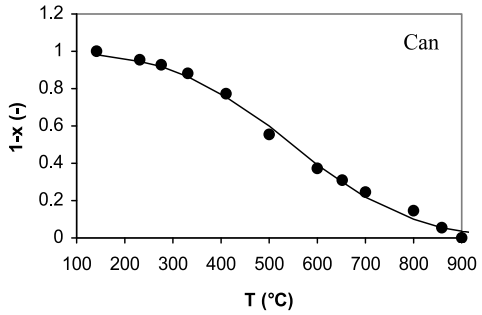
[a]Correlation coefficient between TGA data and DAEM prediction.

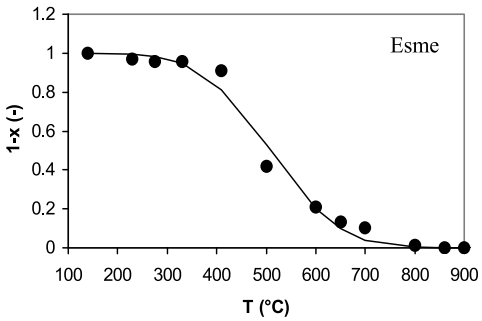
with non-isothermal TGA data in Figure 1. It can be said that there is a good harmony between the DAEM predictions and experimental data. According to the values given in Table 2, the E_o values of Turkish coals vary between 218 and 248 kJ/mol, and the σ values vary between 32 and 70 kJ/mol. The minimum and maximum values are 0.00787 and 0.03673 for the sum of squares of differences (h2), respectively. The maximum and minimum values of correlation coefficient (R2) between TGA data and DAEM prediction are 0.99792 and 0.99194, respectively. Maximum values for both E_o and σ belong to Kemerburgaz coal. Soma1 coal has minimum E_o value and Esme coal has minimum σ value. The average values of calculated kinetic parameters are 232 kJ/mol for E_o and 49 kJ/mol for σ.

Since TGA data may not always be available, correlations that enable calculation of the DAEM parameters in terms of readily available coal characteristics will be extremely useful. Each coal has a distinctive weight loss curve, and the effect of E_o and σ on the shape of this curve is evident. Hence, correlations between E_o and σ of the DAEM and certain properties of coal, which can be easily determined from either the proximate or the elemental analysis of coal, have been investigated. Both single and multivariable correlations were explored on dry basis. A general-purposed mathematical software has been employed for data analysis and deriving of the correlations. The obtained correlations are given in Table 3 and Table 4 together with the mean absolute error (MAE) and the maximum absolute difference (MAD) values.

If an evaluation is made for E_o correlations based on proximate analysis, the MAE values vary from 2.38 to 3.58. The MAD values are between 5.44 and 8.00. For σ correlations, the minimum and maximum values of MAE are 16.58 and 20.69, respectively. The MAD values vary from 32.43 to 53.97. The MAE values of the E_o correlations based on the elemental analysis vary from 2.57 to 3.61. The MAD values are between 6.09 and 7.50. For σ correlations, the MAE values vary from 13.82 and 21.86. The minimum and maximum values of MAD are 37.95 to 60.55, respectively.







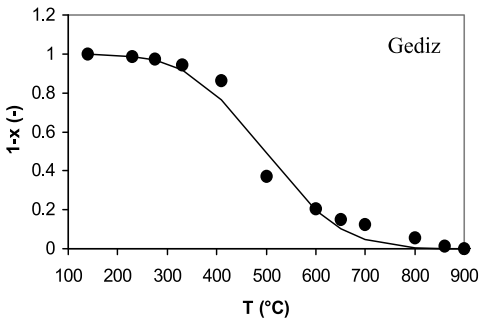
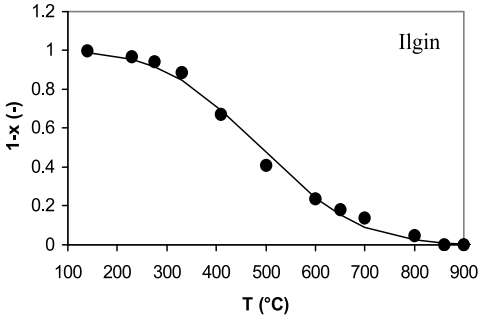
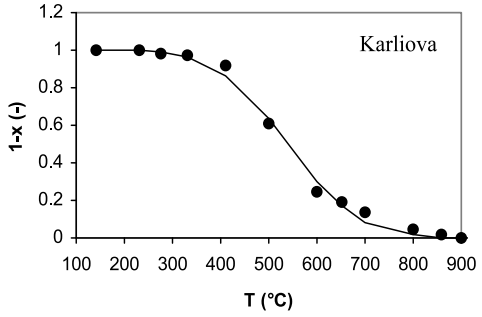
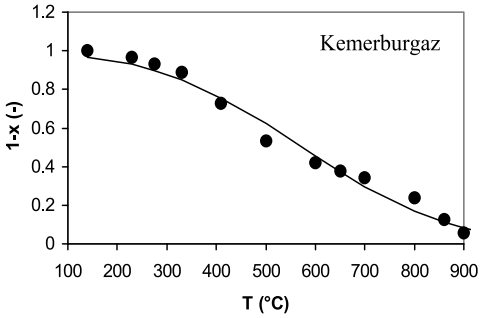


Figure 1. Comparison of weight loss curves calculated from the distributed activation energy model with non-isothermal TGA data (●: TGA, —: DAEM). (*continued*)







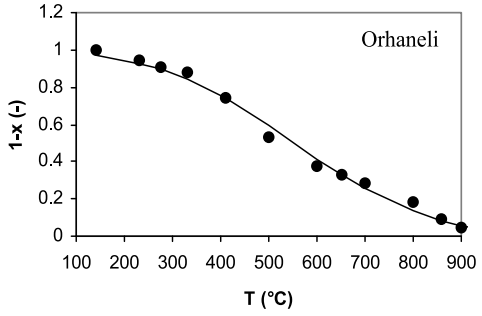
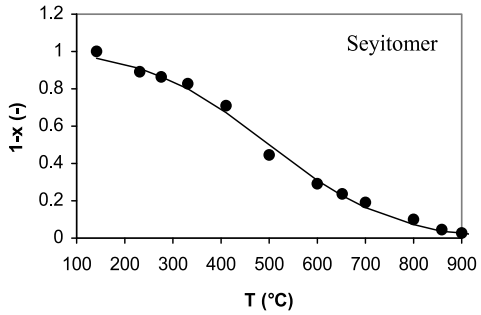
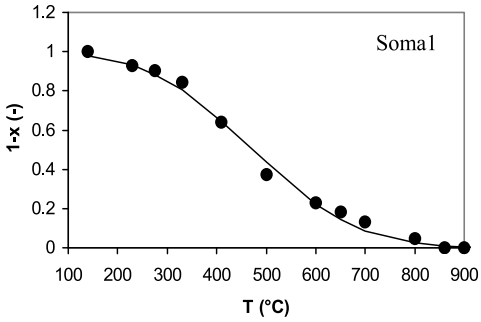
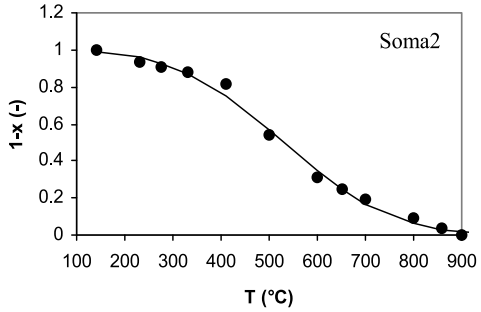


Figure 1. (*Continued*).







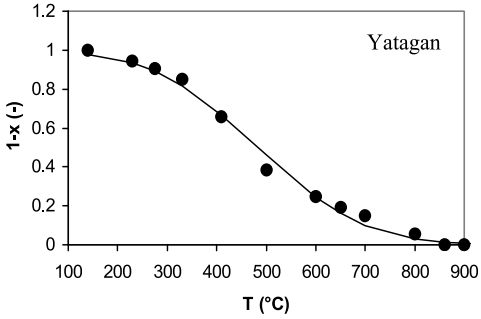


Figure 1. (*Continued*).

Table 3
Correlations for E_o and σ based on proximate analysis

Correlations	MAE, %	MAD, %
$E_o = 259.205 - 0.615316\ \mathrm{VM}$	3.23	7.83
$E_o = -170.819 + 19.2279\ \mathrm{VM} - 0.225099\ \mathrm{VM}^2$	2.46	7.84
$E_o = -643.702 + 52.0276\ \mathrm{VM} - 0.977509\ \mathrm{VM}^2 + 0.00570869\ \mathrm{VM}^3$	2.38	8.00
$E_o = 216.548 + 0.409872\ \mathrm{FC}$	3.09	7.27
$E_o = -196.944 + 33.6066\ \mathrm{FC} - 0.861122\ \mathrm{FC}^2 + 0.00724383\ \mathrm{FC}^3$	2.87	5.44
$E_o = 245.998 - 11.2251\ \mathrm{VM/FC}$	2.87	7.69
$E_o = 280.642 - 117.069\ \mathrm{VM/FC} + 97.3346\ (\mathrm{VM/FC})^2 - 27.1362\ (\mathrm{VM/FC})^3$	2.97	6.34
$E_o = 239.7156 - 0.4014359\ \mathrm{VM} + 0.2647904\ \mathrm{FC}$	2.99	7.90
$E_o = 247.4564 - 11.4949\ \mathrm{VM/FC} - 0.4017221\ \mathrm{VM/A}$	2.88	7.73
$E_o = 247.2477 - 11.77296\ \mathrm{VM/FC} - 0.2236296\ \mathrm{FC/A}$	2.88	7.69
$E_o = 245.5895 - 11.96181\ \mathrm{VM/FC} + 5.717084\ \mathrm{A/(VM + FC)}$	2.88	7.82
$E_o = 232.3982 - 4.734454\ \mathrm{VM/A} + 5.047937\ \mathrm{FC/A}$	2.89	7.91
$E_o = 242.6696 - 1.752953\ \mathrm{VM/A} - 24.27926\ \mathrm{A/(VM + FC)}$	3.58	6.24
$E_o = 212.2881 + 4.70393\ \mathrm{FC/A} + 33.44291\ \mathrm{A/(VM + FC)}$	3.01	7.99
$E_o = 241.4037 - 12.28461\ \mathrm{VM/FC} + 0.9887119\ \mathrm{VM/A} + 13.56139\ \mathrm{A/(VM + FC)}$	2.88	7.90
$E_o = 238.3787 - 10.11955\ \mathrm{VM/FC} + 1.160873\ \mathrm{FC/A} + 14.12712\ \mathrm{A/(VM + FC)}$	2.85	8.00
$\sigma = -5.745174 + 1.191769\ \mathrm{VM} + 0.0733322\ \mathrm{FC}$	17.77	32.43
$\sigma = 17.9521 + 14.12902\ \mathrm{VM/FC} + 4.991066\ \mathrm{VM/A}$	17.59	33.85
$\sigma = 14.36856 + 20.32799\ \mathrm{VM/FC} + 3.85525\ \mathrm{FC/A}$	19.56	37.79
$\sigma = 38.83402 + 15.2574\ \mathrm{VM/FC} - 35.82276\ \mathrm{A/(VM + FC)}$	19.50	32.88
$\sigma = 35.96563 + 11.3287\ \mathrm{VM/A} - 7.112031\ \mathrm{FC/A}$	16.58	33.01
$\sigma = 7.584255 + 9.956469\ \mathrm{VM/A} + 60.13117\ \mathrm{A/(VM + FC)}$	17.92	53.97
$\sigma = 75.65289 - 4.814042\ \mathrm{FC/A} - 59.93784\ \mathrm{A/(VM + FC)}$	20.69	49.75
$\sigma = 8.918785 + 12.95043\ \mathrm{VM/FC} + 7.066207\ \mathrm{VM/A} + 20.23958\ \mathrm{A/(VM + FC)}$	17.13	37.22
$\sigma = 31.45524 + 17.14259\ \mathrm{VM/FC} + 1.187923\ \mathrm{FC/A} - 27.21675\ \mathrm{A/(VM + FC)}$	19.37	32.97

Unfortunately, none of the correlations explored proved to be successful. E_o exhibits small and random fluctuations in the vicinity of approximately 230 kJ/mol, while σ is scattered too much with respect to any of the variables considered.

In some studies (Maki et al., 1997; Miura and Maki, 1998a, 1998b; Burnham and Braun, 1999; McGuinness et al., 1999; Pleasea et al., 2003), new approximations to the DAEM equation were published. On the other hand, some researchers (Vyazovkin and Wight, 1999; Sewry and Brown, 2002; Conesa et al., 2004; Sebastião et al., 2004) published new approximations for modeling thermal decompositions. These approximations should be adapted to Turkish coals.

Table 4
Correlations for E_o and σ based on elemental analysis

Correlations	MAE, %	MAD, %
$E_o = 207.343 + 2.16593$ (C/H)	3.31	7.29
$E_o = 16.1909 + 35.1788$ (C/H) $- 1.40822$ (C/H)^2	3.22	7.30
$E_o = 233.692 - 0.309853$ ((C + H)/O)	3.61	6.09
$E_o = 194.695 + 19.742$ ((C + H)/O) $- 2.63647$ ((C + H)/O)^2 + 0.0982983 ((C + H)/O)^3	2.57	7.50
$E_o = 227.5874 - 0.173215$ (C + H)/O + 1.248154E-02 (C + H)/S + 1.252143 (C + H)/A	3.36	6.71
$E_o = 188.5215 + 4.759371$ C/H $- 0.9291677$ (C + H)/O $-$ 1.003026E-02 (C + H)/S $- 1.496192$ (C + H)/A	3.30	6.91
$E_o = 212.3115 + 1.52764$ C/H + 0.5857993 (C + H)/A	3.29	7.21
$E_o = 208.9392 + 1.981493$ C/H + 1.558241E-02 (C + H)/S	3.34	7.32
$E_o = 189.8425 + 4.59959$ (C/H) $- 0.8946482$ (C + H)/O $-$ 1.494471 (C + H)/A	3.32	6.95
$E_o = 203.2185 + 2.813496$ (C/H) $- 0.6032751$ (C + H)/O $-$ 9.858641E-03 (C + H)/S	3.31	6.90
$E_o = 227.5746 - 0.1855165$ (C + H)/O + 1.373999 (C + H)/A	3.35	6.65
$E_o = 231.8735 - 0.229751$ (C + H)/O + 4.284084E-02 (C + H)/S	3.48	6.47
$E_o = 226.4813 + 1.484811$E-02 (C + H)/S + 1.295798 (C + H)/A	3.34	6.91
$\sigma = 65.22446 - 2.386737$ (C + H)/O $-$ 2.377681E-02 (C + H)/S $- 0.8163315$ (C + H)/A	14.94	47.72
$\sigma = 101.6434 - 4.436894$ C/H $- 1.682005$ (C + H)/O $-$ 2.790307E-03 (C + H)/S + 1.745785 (C + H)/A	13.85	38.46
$\sigma = 144.0131 - 10.22386$ C/H + 5.634998 (C + H)/A	16.64	37.95
$\sigma = 104.0506 - 5.010565$ C/H + 8.397829E-02 (C + H)/S	18.64	60.55
$\sigma = 102.0109 - 4.481343$ (C/H) $- 1.672402$ (C + H)/O + 1.746264 (C + H)/A	13.87	38.52
$\sigma = 84.49469 - 2.166409$ (C/H) $- 2.062263$ (C + H)/O $-$ 2.990561E-03 (C + H)/S	13.82	44.34
$\sigma = 65.2489 - 2.363303$ (C + H)/O $- 1.048463$ (C + H)/A	14.64	49.17
$\sigma = 62.43016 - 2.349879$ (C + H)/O $-$ 4.356948E-02 (C + H)/S	15.47	45.59
$\sigma = 49.9837 + 8.832285$E-03 (C + H)/S $- 0.2147923$ (C + H)/A	21.86	55.32

Only one single heating rate (20 K/min) was used in the TGA analysis. To be able to observe the effect of different heating rates on determination of DAEM parameters for Turkish coals, this study should be repeated with TGA data obtained for different heating rates.

4. Conclusion

Turkish researchers mostly prefer the single-reaction models in the explanation of thermal decomposition process. Sometimes the single-reaction model gives unsuccessful results for the organic decompositions. This may be due to the representation of the large number

of decomposition reactions by only a single reaction. Furthermore, the reason for this may arise from the coal types, experimental condition, and numerical method.

This study shows that the distributed activation energy model (representing multi-reaction model) appears to provide a quantitatively satisfactory description of the devolatilization behavior of Turkish coals. Therefore, the distributed activation energy model should be used in the explanation of thermal decomposition of Turkish coals.

Correlations between E_o and σ of the DAEM and certain properties of coal, which can be easily determined from either the proximate or the elemental analysis of coal, have been investigated. Although each coal has a distinctive weight loss curve, and the effect of E_o and σ on the shape of this curve is evident, apparently there is no correlation between the kinetic parameters of this model and the elemental or proximate analysis of coal.

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References

Anthony, D. B., and Howard, J. B. 1976. Coal devolatilization and hydrogasification. *AIChE J.* 22:625–656.

Ballice, L. 2002. Classification of volatile products evolved from temperature-programmed pyrolysis of Soma-Lignite and Sirnak-Asphaltite from Turkey. *J. Anal. Appl. Pyrolysis* 63:267–281.

Ballice, L., and Saglam, M. 2003. Co-pyrolysis of Goynuk-oil shale and ırnak-asphaltite from Turkey and analysis of co-pyrolysis products by capillary GC total stream sampling technique. *Fuel* 82:511–522.

Bilge, Z. D. 1988. *Investigation of volatile matter behavior in a fluidized bed*. Ph.D. Thesis, Yildiz Technical University, Istanbul.

Brown, M. E. 1988. *Introduction to Thermal Analysis: Techniques and Applications.* New York: Chapman and Hall.

Brown, M. E., Maciejewski, M., Vyazovkin, S., Nomen, R., Sempere, J., Burnham, A., Opfermann, J., Strey, R., Anderson, H. L., Kemmler, A., Keuleers, R., Janssens, J., Desseyn, H. O., Li, C,-R., Tang, T. B., Roduit, B., Malek, J., and Mitsuhashi, T. 2000. Computational aspects of kinetic analysis. Part A: The ICTAC kinetics project data, methods, and results. *Thermochim. Acta* 355:125–143.

Burnham, A. K. 2000. Computational aspects of kinetic analysis. Part D: The ICTAC kinetics project—Multi-thermal-history model-fitting methods and their relation to isoconversional methods. *Thermochim. Acta* 355:165–170.

Burnham, A. K., and Braun, R. L. 1999. Global kinetic analysis of complex materials. *Energy Fuels* 13:1–22.

Ceylan, K., and Olcay, A. 1998. Kinetic rate models for dissolution of Turkish lignites in tetralin under nitrogen or hydrogen atmospheres. *Fuel Process. Technol.* 53:183–195.

Ceylan, K., Karaca, H., and Onal, Y. 1999. Thermogravimetric analysis of pretreated Turkish lignites. *Fuel* 78:1109–1116.

Ciuryla, V. T., Weimer, R. F., Bivans, D. A., and Motika, S. A. 1979. Ambient-pressure thermogravimetric characterization of four different coals and their chars. *Fuel* 58:748–754.

Conesa, J. A., Caballero, J. A., and Reyes-Labarta, J. A. 2004. Artificial neural network for modeling thermal decompositions. *J. Anal. Appl. Pyrolysis* 71:343–352.

Degirmenci, L., and Durusoy, T. 2005. Effect of heating rate and particle size on the pyrolysis of Göynük oil shale. *Energy Sources* 27:787–795.

Duz, M. Z., Tonbul, Y., Baysal, A., Akba, O., Saydut, A., and Hamamci, C. 2005. Pyrolysis kinetics and chemical composition of Hazro coal according to the particle size. *J. Therm. Anal. Calorim.* 81:395–398.

Ekinci, E., Yalkın, G., Atakul, H., and Senatalar, A.-E. 1988. The combustion of volatiles from some Turkish coals in a fluidized bed. *J. Inst. Energy* 155:189–191.

Guldogan, Y., Bozdemir, T., and Durusoy, T. 2001b. Pyrolysis kinetics of blends of Gediz lignite with Denizli peat. *Energy Sources* 23:393–399.

Guldogan, Y., Durusoy, T., and Bozdemir, T. 2002. Effects of heating rate and particle size on pyrolysis kinetics of Gediz lignite. *Energy Sources* 24:753–760.

Guldogan, Y., Ozbas-Bozdemir, T., and Durusoy, T. 2000. Effect of heating rate on pyrolysis kinetics of Tuncbilek lignite. *Energy Sources* 22:305–312.

Gunes, M., and Gunes, S. 2002. A direct search method for determination of DAEM kinetic parameters from non-isothermal TGA data (note). *Appl. Math. Comput.* 130:619–628.

Gunes, M., and Gunes, S. 2005. A study on thermal decomposition kinetics of some Turkish coals. *Energy Sources* 27:749–759.

Gunes, S. 1997. *Characterization of volatiles components of Turkish coals and modeling of devolatilization.* Ph.D. Thesis, Yildiz Technical University, Istanbul.

Guruz, G. A., Uctepe, U., and Durusoy, T. 2004. Mathematical modeling of thermal decomposition of coal. *J. Anal. Appl. Pyrolysis* 71:537–551.

Kizgut, S., and Yilmaz, S. 2004. Characterization and non-isothermal decomposition kinetics of some Turkish bituminous coals by thermal analysis. *Fuel Process. Technol.* 85:103–111.

Kok, M. V. 2003. Coal pyrolysis: Thermogravimetric study and kinetic analysis. *Energy Sources* 25:1007–1014.

Kucukbayrak, S. 1993. Volatile release profiles of some Turkish lignites. *Thermochim. Acta* 216: 131–136.

Kucukbayrak, S., Haykiri-Acma, H., Ersoy-Mericboyu, A., and Yaman, S. 2001. Effect of lignite properties on reactivity of lignite. *Energy Convers. Manage.* 42:613–626.

Lee, T. V., and Beck, S. R. 1984. A new integral approximation formula for kinetic analysis of non-isothermal TGA data. *AIChE J.* 30:517–519.

Maciejewski, M. 2000. Computational aspects of kinetic analysis. Part B: The ICTAC Kinetics Project—The decomposition kinetics of calcium carbonate revisited, or some tips on survival in the kinetic minefield. *Thermochim. Acta* 355:145–154.

Maki, T., Takatsuno, A., and Miura, K. 1997. Analysis of pyrolysis reactions of various coals including Argonne premium coals using a new distributed activation energy model. *Energy Fuels* 11:972–977.

McGuinness, M. J., Donskoi, E., and McElwain, D. L. S. 1999. Asymptotic approximations to the distributed activation energy model. *Appl. Math. Lett.* 12:27–34.

Miura, K., and Maki, T. 1998a. A simple method for estimating f(E) and k0(E) in the distributed activation energy model. *Energy Fuels* 12:864–869.

Miura, K., and Maki, T. 1998b. Simplified method to estimate f(E) in distributed activation energy model for analyzing coal pyrolysis reaction. *J. Chem. Eng. Jpn.* 31:228–235.

Pitt, G. J. 1962. The kinetics of the evolution of volatile products from coal. *Fuel* 41:267–274.

Pleasea, C. P., McGuinness, M. J., and McElwain, D. L. S. 2003. Approximations to the distributed activation energy model for the pyrolysis of coal. *Combust. Flame* 133:107–117.

Roduit, B. 2000. Computational aspects of kinetic analysis. Part E: The ICTAC Kinetics Project—Numerical techniques and kinetics of solid state processes. *Thermochim. Acta* 355:171–180.

Saxena, S. C. 1990. Devolatilization and combustion characteristics of coal particles. *Prog. Energy Combust. Sci.* 16:55–94.

Sebastião, R. C. O., Braga, J. P., and Yoshida, M. I. 2004. Competition between kinetic models in thermal decomposition: Analysis by artificial neural network. *Thermochim. Acta* 412:107–111.

Sewry, J. D., and Brown, M. E. 2002. "Model-free" kinetic analysis? *Thermochim. Acta* 390: 217–225.

Sinag, A. 2004. The influence of pyrolysis conditions on the reactivity of Soma-Isiklar lignite (Turkey). *Energy Sources* 26:127–134.

Solomon, P. R., Serio, M. A., and Suuberg, E. M. 1992. Coal pyrolysis: Experiments, kinetic rates, and mechanisms. *Prog. Energy Combust. Sci.* 18:133–220.

Suuberg, E. M., Peters, W. A., and Howard, J. B. 1978. Product composition and kinetics of lignite pyrolysis. *Ind. Eng. Chem. Process. Des. Dev.* 17:37–46.

Thakur, D. S., and Nuttall Jr, H. E. 1987. Kinetics of pyrolysis of Moroccan oil shale by thermogravimetry. *Ind. Eng. Chem. Res.* 26:1351–1356.

Tia, S., Bhattacharya, S. C., and Wibulswas, P. 1991. Thermogravimetric analysis of Thai lignite. I. Pyrolysis kinetics. *Energy Convers. Manage.* 31:265–276.

Urkan, M. K. 1990. *Combustion of Turkish coals in a fluidized bed and investigation of volatile matter combustion behavior.* Ph.D. Thesis, Yildiz Technical University, Istanbul.

Urkan, M. K., and Arıkol, M. 1994. Burning times of volatiles from Turkish coals during fluidized bed combustion. *Fuel* 73:768–772.

Urkan, M. K., Bilge, D., Arıkol, M., and Heperkan, H. 1987. Devolatilization of some Turkish lignites in a fluidized bed. *Proceedings of the 1987 International Conference on Coal Science*, Moulijn, J. A. et al. (Eds.). Amsterdam: Elsevier, pp. 643–646.

Vyazovkin, S. 2000. Computational aspects of kinetic analysis. Part C: The ICTAC Kinetics Project—The light at the end of the tunnel? *Thermochim. Acta* 355:155–163.

Vyazovkin, S., and Wight, C. A. 1999. Model-free and model-fitting approaches to kinetic analysis of isothermal and non-isothermal data. *Thermochim. Acta* 340–341:53–68.

Nomenclature

a	initial temperature, K
A	ash, %
b	heating rate, K/s
C	carbon content, %
E	activation energy, kJ/mol
E_o	mean of activation energy distribution, kJ/mol
FC	fixed carbon, %
H	hydrogen content, %
h2	Sum of squares of differences, –
k_o	frequency factor, 1/s
M	moisture, %
n	number of data points
N	nitrogen content, %
R	universal gas constant, 8.314E-3, kJ/mol-K
$R2$	correlation coefficient, –
S	sulfur content, %
t	time, s
T	absolute temperature, K
w	sample weight, mg
x	mass fraction of releasing volatiles, –
σ	standard deviation of the activation energy distribution, kJ/mol

Subscripts

i	at initial time
f	at final time
t	at time t

Abbreviations

DAEM	distributed activation energy model
MAD	maximum absolute difference
MAE	mean absolute error
TGA	thermogravimetric analysis
VM	volatile matter