

Pyrolysis Kinetics of Turkish Bituminous Coals by Thermal Analysis

İffet YAKAR ELBEYLİ, Sabriye PİŞKİN

Yıldız Technical University, Department of Chemical Engineering, İstanbul-TURKEY
e-mail: ielbeyli@yildiz.edu.tr

Hale SÜTCÜ

Zonguldak Karaelmas University, Department of Chemistry, Zonguldak-TURKEY

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Abstract

Simultaneous thermogravimetry-differential thermal analysis (TG-DTA) was used to study the pyrolysis kinetics of Turkish bituminous coals. Thermogravimetry (TG) and derivative thermogravimetry (DTG) were employed to measure the weight changes and rates of weight loss, which were used for comparison of the thermal behaviour of several coals and calculation of their kinetic parameters. Coal samples were heated in TG-DTA apparatus in an inert atmosphere (100 ml min⁻¹nitrogen) at a temperature range of 25-1000 °C. The activation energy (E_a) and pre-exponential factor (A) were calculated from the experimental results by using an Arrhenius-type kinetic model. The data indicate that the pyrolysis of coals is a 1-stage process. The decomposition stage (350-700 °C) has a best fit with first-order kinetics with $E_a = 65-97$ kJ mol⁻¹.

Key words: Pyrolysis, coal, DTA, TG, kinetic.

Introduction

Thermal analysis has been widely used in recent years for the investigation of combustion and pyrolysis behaviours of fossil fuels such as coals, oil shales and tar sands (Kural, 1998). The thermal properties of coal play a significant role in revealing certain of its specific properties and its most appropriate uses are in industry and the impacts of coal combustion on environmental pollution (Kök and Pamir, 2000). Methods such as differential thermal analysis (DTA), thermogravimetric analysis (TG), dynamic microcalorimetric analysis (DMA) and swelling index (SI) measurements have been used for many years in order to investigate the thermal properties of coal.

The chemistry of coal pyrolysis includes the decomposition of individual functional groups to produce light gas species, and the decomposition of the macromolecular network to produce smaller fragments. Network decomposition is a complicated mixture of bridge breaking, crosslinking, hydrogen trans-

fer, substitution etc. When certain pyrolysed bituminous coals pass through a plastic state they successively soften, swell and resolidify into a cellular coke. Semicoke is converted into coke at high temperatures. The formation of a regular structure in bituminous coals is observed at temperatures above 700 °C (Berkowitz, 1985; Ladner, 1998).

Coal pyrolysis, which involves numerous complex reactions, is very important in coal conversion processes. As the temperature increases, considerable changes occur in the coal structure and result in the formation of the solid residue of pyrolysis: coke or char (Elder and Harris, 1984; Lazaro *et al.*, 1998; Ceylan *et al.*, 1999; Jaber and Probert, 2000). Solid, liquid and gaseous products are formed during the pyrolysis reactions and some of these reactions are accompanied by weight, calorific value and temperature changes. TG of coal samples has been extensively used to determine the characteristics of devolatilisation and kinetic parameters.

Pyrolysis kinetics has been studied for some

years. Elder and Harris (1984) investigated the thermal characteristics of Kentucky bituminous coals during pyrolysis in an inert atmosphere. They determined the exothermic reaction at a range of 300 to 500 °C, where the major weight loss occurs and which has been associated with the primary carbonisation process and the development of a plastic state. At the end of this stage, secondary gasification starts and this is responsible for coke formation. It was found that the total activation energy for the 2 steps was 198-200 kJ mol⁻¹. Devolatilisation of bituminous coals was studied in a fluidised bed reactor at a temperature range of 500 to 900 °C by Puente *et al.* (1998). The volatile matter release profile of fresh coal can be described using 3 stages: Stage I (250-475 °C) in which mainly light species are liberated; Stage II (475-575 °C), characteristic of bituminous coals in which high molecular weight species (tar) and hydrocarbons (primary gases) are evolved, which may lead to melting (metaplast); and Stage III (>575 °C) in which secondary gases are produced while undergoing ring condensation leading to the formation of coke. With the assumption of a first-order reaction, the activation energy is obtained as 10.5-46.4 kcal mol⁻¹.

The purpose of this study was to investigate the kinetics of the pyrolysis of Turkish bituminous coals and their structural changes during thermal treatment.

Materials and Methods

Bituminous coal samples were collected from different coal mines in Zonguldak, in north-west Turkey. The coal samples were from Armutcuk, Amasra, Karadon, Azdavay and Kurucaşile. These samples were crushed and ground mechanically. After being washed with tap water, they were oven-dried at 105 °C for 2 h. Table 1 shows the results of proximate and ultimate analyses of the coals used in this study.

Coal samples with a particle size of -200 µm were used for the TG and DTG analyses. For experimental parameters, 10 mg coal samples a nitrogen atmosphere (100 ml min⁻¹), and a linear heating rate of 10 °C min⁻¹ were used. All experiments were performed over a temperature range of 25 to 1000 °C using platinum crucibles. Prior to the experiments, the TG apparatus was calibrated via the melting points of indium (156.6 °C), tin (231.9 °C), lead (327.5 °C), zinc (419.6 °C), aluminum (660.2 °C) and gold (1063 °C) standards under the same conditions as for the samples. α alumina was used as reference material in all experiments. The weight loss (TG signal) and the rate of weight loss (DTG signal) as a function of time or temperature were recorded, while the coals were subjected to a computer-controlled temperature programme. The TG and DTG curves were obtained by a Setaram Labsys model instrument.

Table 1. Characterisation of bituminous coal samples.

Coal Samples	Armutcuk	Amasra	Karadon	Azdavay	Kurucaşile
Proximate analysis, wt ^a .%					
Ash	4.36	7.99	8.81	11.8	5.22
Volatile matter	32.81	36.24	23.62	28.44	38.07
Fixed carbon	62.83	55.77	67.57	59.76	56.71
Ultimate Analysis ^b (%)					
C	86.27	77.87	88.83	85.19	85.57
H	4.67	5.19	4.54	5.03	5.07
N	1.19	1.06	0.73	0.89	1.11
O	7.24	5.22	5.27	5.27	7.23
S	0.63	0.66	0.63	0.63	1.02
H/C (atomic)	0.65	0.8	0.61	0.61	0.71
O/C (atomic)	0.06	0.15	0.04	0.04	0.06
Calorific value ^a (MJ kg ⁻¹)	32.91	32.63	30.86	30.86	32.91

^adry basis

^bdry-ash free basis

TG (on a percentage basis) and DTG curves for Zonguldak bituminous coals from Armutcuk, Amasra, Karadon, Azdavay and Kurucaşile, at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ in an inert atmosphere are represented in Figures 1-5 and the pyrolysis stages are shown in Table 2.

Kinetics of thermal decomposition

There are a number of approaches for modelling the complex pyrolysis process. The simplest is the em-

pirical model, which employs global kinetics, where the Arrhenius expression is used to correlate the rates of mass loss with temperature (Arenillas *et al.*, 2001). The pyrolysis process of coals can be represented by the following reaction:

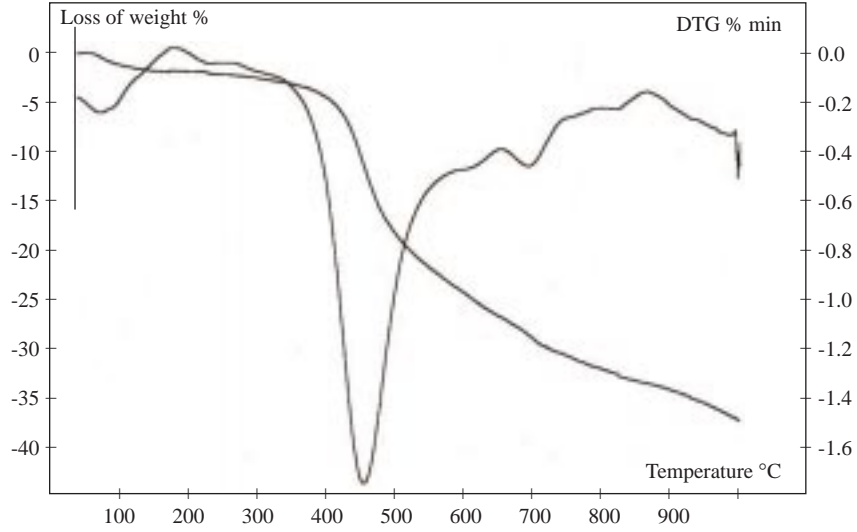
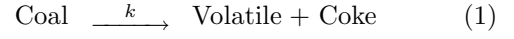


Figure 1. TG-DTG curve for Armutcuk coal.

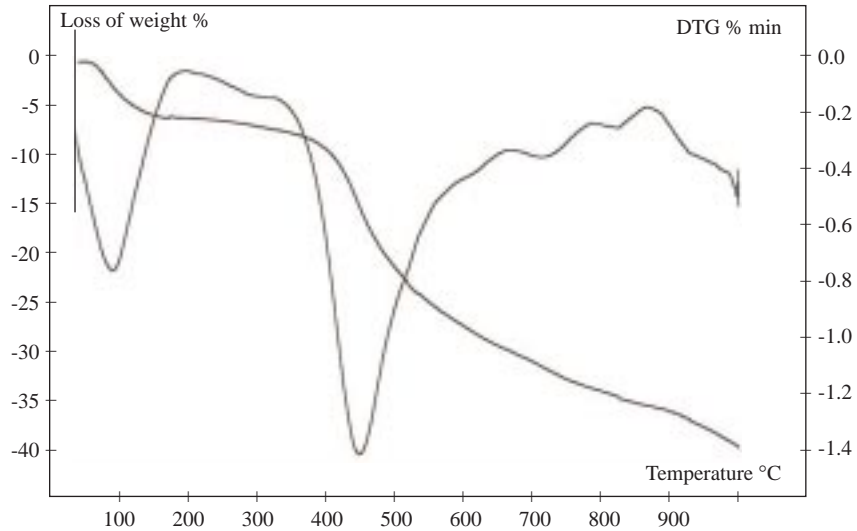


Figure 2. TG-DTG curve for Amasra coal.

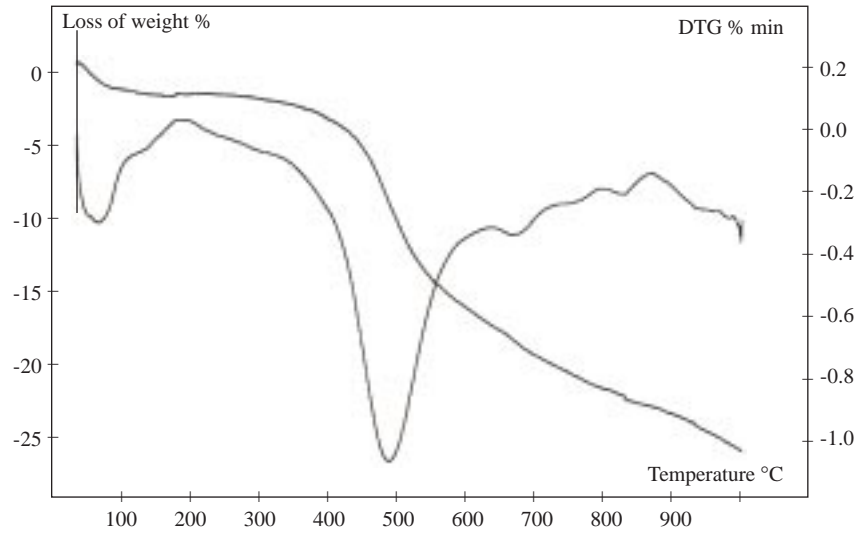


Figure 3. TG-DTG curve for Karadon coal.

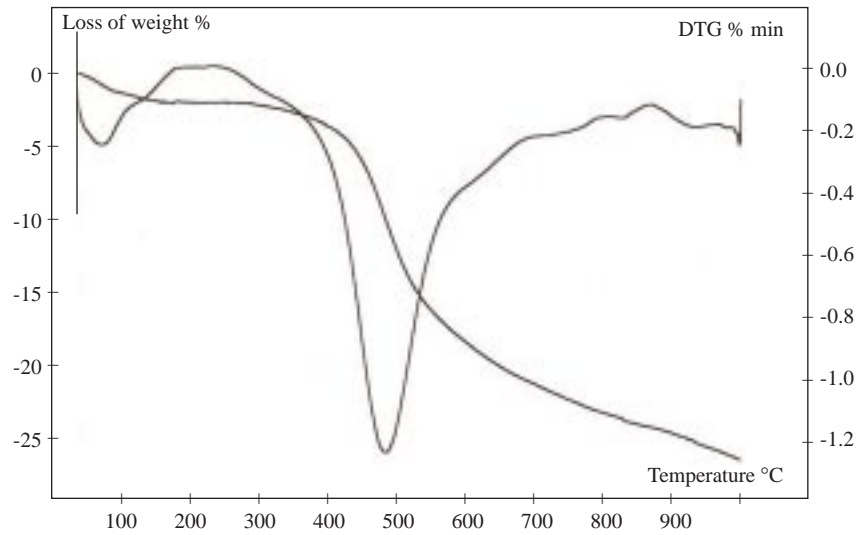


Figure 4. TG-DTG curve for Azdavay coal.

For analysing the kinetics of TG/DTG data, the model assumes that the rate of weight loss of the total sample is dependent only on the rate constant, the remaining weight of the sample and its temperature with a reaction order of unity.

The kinetic parameters of the thermal decomposition reactions were calculated by using an Arrhenius-type kinetic model assuming that there is a first-order reaction (Kök and Pamir, 2000). The

kinetic analysis of non-isothermal pyrolysis, in general, is based on the following equations:

$$\frac{dW}{dt} = k \cdot W^n \quad (2)$$

$$k = A_r \exp\left(\frac{-E}{RT}\right) \quad (3)$$

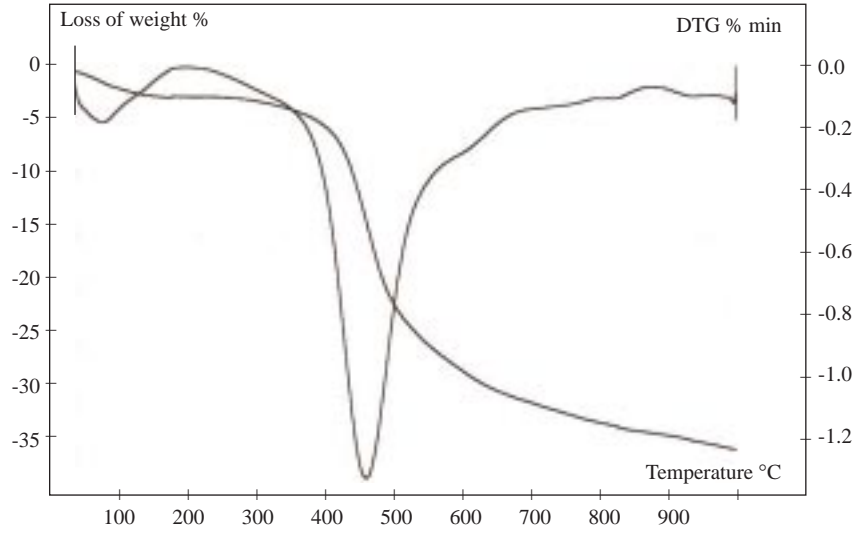


Figure 5. TG-DTG curve for Kurucaşile coal.

Table 2. Pyrolysis stages for Turkish bituminous coals determined from TG-DTG data.

Pyrolysis stages	Coal Samples				
	Armutcuk	Amasra	Karadon	Azdavay	Kurucaşile
Amount of moisture (>200 °C) (%)	1.90	5.52	2.18	1.92	2.17
Temperature region of active decomposition (°C)	350-600	330-680	320-650	360-700	350-700
Temperature region of secondary gasification (°C)	600-1000	680-1000	650-1000	700-1000	700-1000

Assuming first order kinetics ($n = 1$),

$$\frac{dW}{dt} = A_r \exp\left(\frac{-E}{RT}\right) \cdot W \quad (4)$$

taking the logarithm of both sides,

$$\log\left[\left(\frac{dW}{dt}\right) \cdot \left(\frac{1}{W}\right)\right] = \log A_r - \frac{E}{2.303RT} \quad (5)$$

where dW/dt is the rate of weight change of the reacting material in $\% \text{ min}^{-1}$, A_r is the Arrhenius constant or pre-exponential factor in 1 min^{-1} , E is the activation energy in kJ mol^{-1} , T is the temperature in K , n is the reaction order and R is the gas constant in $8.314 \text{ J mol}^{-1}\text{K}^{-1}$.

In the model, the plot of $\log[(dW/dt) \cdot (1/W)]$ against $1/T$ is a straight line with a slope of $-E/2.303R$. The magnitude of the slope can be used to calculate the activation energy (E). The pre-exponential factor (A) can be calculated from the

intercept. The assumption of a first-order reaction appears reasonable as shown in Figure 6. The main temperature range of volatile evolution ($350\text{-}600 \text{ }^\circ\text{C}$) was always taken into account in the calculation and a regression factor, R^2 , in the order of 0.98 was obtained in all cases.

Results and Discussion

The TG-DTG curves of the Turkish bituminous coals from Zonguldak indicate that pyrolysis of coals occurs in 3 main temperature regions. DTG curves of all samples from Armutcuk, Amasra, Azdavay, Karadon and Kurucaşile, show the same trend in thermal behaviour in having 2 or 3 peaks. Table 2 shows the pyrolysis stages and decomposition temperatures of bituminous coals.

As can be seen from the Figures 1-5, the first small peak which occurs between 60 and 200 °C is due to the elimination of moisture. After the loss of

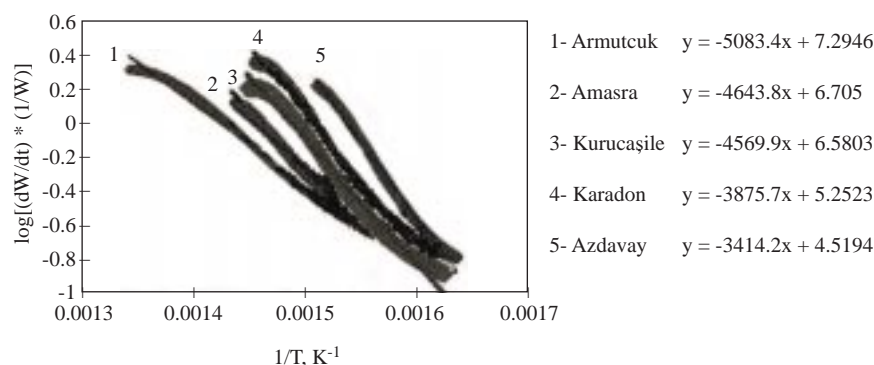


Figure 6. Plot of first-order equation for TG curves of different bituminous coals.

moisture in the temperature region of 200 to 350 °C, all coals start to lose small amounts of pyrolysis water from decomposing phenolic structures and oxides of carbon from carboxylic and carbonyl groups (Elder and Harris, 1984). At temperatures below 350-400 °C, different processes take place prior to primary pyrolysis, i.e. disruption of hydrogen bonds, vaporisation and transport of the non-covalently bonded molecular phase (Ladner, 1998).

The second peak, where essential weight loss occurs in the range of 350 to 700 °C is related to primary devolatilisation, during which carbon, hydrogen and oxygen compounds are released. At 350 °C primary carbonisation starts, initially with the release of carbon dioxide and hydrogen. Along with the increase in temperature, methane and other lower aliphatics are evolved together with hydrogen, carbon monoxide and alkyl aromatics (Elder and Harris, 1984).

Primary devolatilisation leads to the generation of tars and light oils between T_d (decomposition temperature) and 600 °C. Secondary degasification or active decomposition results in the evolution of a variety of hydrocarbon gases, elemental hydrogen and oxides of carbon over an extended temperature range beyond 600 - 700 °C (Berkowitz, 1985). The third

DTG peak is observed at 700 °C in the DTG curves of the Armutcuk, Amasra and Karadon coal samples. At temperatures higher than 700 °C, the reactions take place with condensation of the carbon matrix and with the evolution of H_2 .

The curves of all coal samples show slight differences in peak temperatures depending on the mineral matter and carbon contents shown in Table 1. The characteristic temperatures are given in Table 3.

It can be seen from Table 3 that the maximum devolatilisation temperatures are about 450-490 °C for the higher temperature region as seen in Figures 1-5. Similar results have been reported by other researchers (Puente *et al.*, 1998; Matuschek and Ketrup, 1999; Arenillas *et al.*, 2001;). The temperatures of the maximum rate of weight loss in the higher temperature region may be used as an indicator of coal reactivity in pyrolysis or devolatilisation.

The activation energy and pre-exponential factor values were obtained for secondary pyrolysis from the formation of light aliphatic hydrocarbons during the pyrolysis of coals. The results obtained from the Arrhenius model indicate these kinds of compounds, which are produced at temperatures of 350-600 °C. The temperature of the maximum rate of mass loss,

Table 3. Characteristic pyrolysis temperatures, volatile matter content and kinetic parameters for bituminous coals.

Coal Type	$T_1 = T_d$ (°C)	T_{max} (°C)	T_2 (°C)	Max. mass loss (% min ⁻¹)	E (kJ mol ⁻¹)	A (1 min ⁻¹)	R ²
Armutcuk	350	460	600	1.710	97.3	1.97×10^7	0.9914
Amasra	330	450	680	1.373	88.9	5.07×10^6	0.9933
Karadon	320	490	650	1.010	74.2	1.79×10^5	0.9875
Azdavay	360	485	700	1.210	65.3	0.33×10^5	0.9854
Kurucaşile	350	463	700	2.030	87.5	3.80×10^6	0.9816

T_{max} , the initial and final temperatures of volatile matters, T_1 and T_2 , activation energy, E , and the pre-exponential factor, A , are shown in Table 3.

Table 3 indicates that T_{max} values are different for the 5 coals, and the increase in T_{max} is in the order Amasra, Armutçuk, Kurucaşile, Azdavay and Karadon. Activation energy values range from 65 to 97 kJ mol⁻¹ in bituminous coals. In conclusion, the TG-DTG curves indicate that Zonguldak bituminous coals have the same thermal properties, but

that Azdavay and Kurucaşile coals exhibit different behaviours from those of the other coals.

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References

- Arenillas, A., Rubiera, F., Pevida, C. and Pis J.J., "A Comparison of Different Methods for Predicting Coal Devolatilisation Kinetics", *Journal of Analytical and Applied Pyrolysis*, 58-59, 685-701, 2001.
- Berkowitz N., *Coal Science and Technology 7, The Chemistry of Coal*. Elsevier, New York, 223, 1985.
- Ceylan, K., Karaca, H. and Önal, Y., "Thermogravimetric Analysis of Pretreated Turkish Lignites", *Fuel*, 78, 1109-1116, 1999.
- Elder, J.P. and Harris, M.B., "Thermogravimetry and Differential Scanning Calorimetry of Kentucky Bituminous Coals", *Fuel*, 63, 262-267, 1984.
- Jaber, S.D. and Probert., J.O., "Non-Isothermal Thermogravimetry and Decomposition Kinetics of Two Jordanian Oil Shales under Different Processing Conditions", *Fuel Processing Technology*, 63, 57-70, 2000.
- Kök, M.V. and Pamir, M.R., "Comparative Pyrolysis and Combustion Kinetics of Oil Shales", *Journal of Analytical and Applied Pyrolysis*, 55, 185-194, 2000.
- Kök M.V., Özbaş, E., Karacan, O. and Hiçyılmaz, C., "Effect of Particle Size on Coal Pyrolysis", *Journal of Analytical and Applied Pyrolysis*, 45, 103-110, 1998.
- Kural, O., *Coal*, İstanbul Technical University, İstanbul, Turkey, 1994.
- Ladner, W.R., "The Products of Coal Pyrolysis: Properties, Conversion and Reactivity", *Fuel Processing Technology*, 20, 207-222, 1988.
- Lazaro, M.J., Moliner, R. and Suelves, I., "Non-Isothermal Versus Isothermal Technique to Evaluate Kinetic Parameters of Coal Pyrolysis", *Journal of Analytical and Applied Pyrolysis*, 47, 111-125, 1998.
- Matuschek, G. and Kettrup, A.A., "Thermal Analysis/Mass Spectrometry as a Tool for Studying Environmental Pollution by Coal Gasification", *Journal of Analytical and Applied Pyrolysis*, 51, 223-237, 1999.
- Puente, G., Marban, G., Fuente, E. and Pis. J.J., "Changes in the Structure of Coals of Different Rank Due to Oxidation—Effects on Pyrolysis Behaviour", *Journal of Analytical and Applied Pyrolysis*, 47, 33-42, 1998.
- Podder, J., Hossain, T., and Mannan, Kh.M., "An Investigation into the Thermal Behaviour of Bangladeshi Coals", *Thermochimica Acta*, 255, 221-226, 1995.