

Pyrolysis kinetics of blends of Tunçbilek lignite with Denizli peat

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Received 26 October 1998; accepted 16 March 1999

Abstract

Tunçbilek lignite and Denizli peat and several peat–lignite blends were pyrolyzed in a thermobalance apparatus at atmospheric pressure. Experiments were carried out dynamically by increasing the temperature from 25°C to 900°C with a heating rate of 20°C/min under an argon atmosphere. Differential thermogravimetric data were analyzed by a reaction rate model assuming first-order kinetics. Effect of blending ratio of peat and lignite on the pyrolysis kinetics was investigated. Kinetic parameters were determined and the results was discussed. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Tunçbilek lignite; Denizli peat; Pyrolysis; Thermogravimetry

1. Introduction

Coal is a complex organic polymer consisting of aromatic clusters of several fused rings strung together by assorted hydrocarbon and heteroatom (O, N, S) linkages. Heating causes the structure to decompose, the weaker bonds rupturing at lower temperatures and the stronger ones at higher temperatures, and the fragments that are volatile attempt to escape from the particle. Some of the fragments are highly reactive free radicals subject to a variety of secondary reactions such as cracking and repolymerization. Products that are obtained through carbonization depend on coal composition, carbonization temperature and the heating rate [1–5].

Geologically, peat is the youngest and least altered member of the combustible rocks. Compared to the other fossil fuels, peat is characterized by the lowest content of fixed carbon along with the highest content

of volatile constituents. Peat is an acidic mixture of dead and decomposed, mainly vegetable, matter which forms in boggy areas. Peat is formed under exclusion of atmospheric oxygen by the action of water by a reduction process. The speed of formation depends on the climatic conditions. The humidification process of the bog plants, the coalification, starts as a biochemical process to form peat and continues at a much slower rate to ultimately form lignite. Up to this stage, cellulose, lignin, suberin, cutin, and sporopollenins can survive in the vegetable matter. The content of cellulose decreases with increasing degree of decomposition, whereas all others increase. A typical elemental analysis (in wt%) of raised-bog peat shows the following range: carbon, 50–60; oxygen, 30–45; hydrogen, 5.0–6.5; nitrogen, 0.5–2.0; sulfur, 0.10–0.5; phosphorus, 0.008–0.025 [6].

Pyrolysis kinetics have been studied over the years by several investigators. Thermal analysis techniques have been applied very successfully to studies of the pyrolysis of fossil fuels in the last two decades [7–10].

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Historically, differential thermal analysis (DTA) was the first thermoanalytical tool used in studying coal pyrolysis [11,12]. Although various investigators have observed similar qualitative effects for coals of the same rank, there is little quantitative data available. The use of thermogravimetry (TG) in coal research was pioneered by Van Krevelen et al. [13–15]. Rosenvald and Dubow [16] analyzed the pyrolysis of 21 bituminous coal samples by DSC and TGA. Three regions of endothermic activity in DSC curves were determined in this study. Mahajan et al. [17] used DSC and TG to study coal pyrolysis employing instrumentation designed for use under a high pressure, 5.6 MPa, flowing helium atmosphere.

The thermal degradation of coal is too complex to be described by an individual chemical reaction. Many techniques such as TG analysis, gas chromatography, IR spectroscopy and mass spectroscopy have been used to study coal conversion at elevated temperatures.

Generally there are two main approaches used in the kinetic analysis. The first approach describes the pyrolysis kinetics by analyzing the gases yielded by individual chemical reactions. The parameters evaluated are explicit, but high-quality analytical equipments are required [18].

The second approach analyses pyrolysis as a whole. The rate of devolatilization of a sample is registered thermogravimetrically. The standard kinetic model for isothermal conditions of Van Krevelen and Schuyer [19], and Chermin and Van Krevelan [20], assuming three successive stages of pyrolysis, is developed. First-order kinetics were assumed in the model, but other workers have suggested that the pyrolysis might be of order >2 [21,22].

The objective of this research was to investigate the pyrolysis kinetics of a lignite and a peat, and their blends.

2. Experimental

2.1. Materials

Tunçbilek lignite and Denizli peat from the Aegean area of Turkey were used in this study. The proximate and ultimate analyses of the Tunçbilek lignite and Denizli peat are given in Table 1.

Table 1
Analyses of the Tunçbilek lignite and Denizli peat

| Proximate analysis (%) | Tunçbilek lignite | Denizli peat |
|---------------------------|-------------------|--------------|
| Moisture | 4.1 | 6.9 |
| Volatile matter | 38.3 | 73.5 |
| Ash | 34.8 | 10.4 |
| Fixed carbon | 22.8 | 9.2 |
| Ultimate analysis (daf %) | | |
| Carbon | 71.0 | 50.5 |
| Hydrogen | 5.0 | 5.4 |
| Sulfur | 1.9 | 0.5 |
| Nitrogen | 2.3 | 2.4 |
| Oxygen | 19.8 | 41.2 |

Carbon and hydrogen contents were determined by ‘‘Heraeus Combustion Apparatus, Type Standard for Microanalytical Determination’’ and nitrogen by Kjeldahl instrument. Total sulfur was determined by the Eschka method according to ASTM D3177.

2.2. Apparatus and procedure

The experiments were performed in Setaram TG DTA 92 thermobalance with which the sample weight loss TG signal and rate of weight loss [derivative thermogravimetric (DTG) signal] as functions of time or temperature were recorded continuously under dynamic conditions. The pyrolysis reaction was conducted under an argon atmosphere. An argon flow rate of 42 ml/min was used to keep the effect of mass transfer at a minimum. All pyrolysis experiments were conducted at atmospheric pressure.

The other experimental conditions were as follows: Interval of pyrolysis temperature: 25–900°C; heating rate: 20°C/min; particle size: ≈ 200 μm ; initial sample weight: ≈ 22 mg. Experiments were performed twice for repeatability.

3. Results and discussion

3.1. Individual feedstocks

TG analysis was applied to determine the pyrolysis kinetics of each feedstock. The TG and DTG curves of the Tunçbilek lignite and Denizli peat are shown in Figs. 1 and 2, respectively.

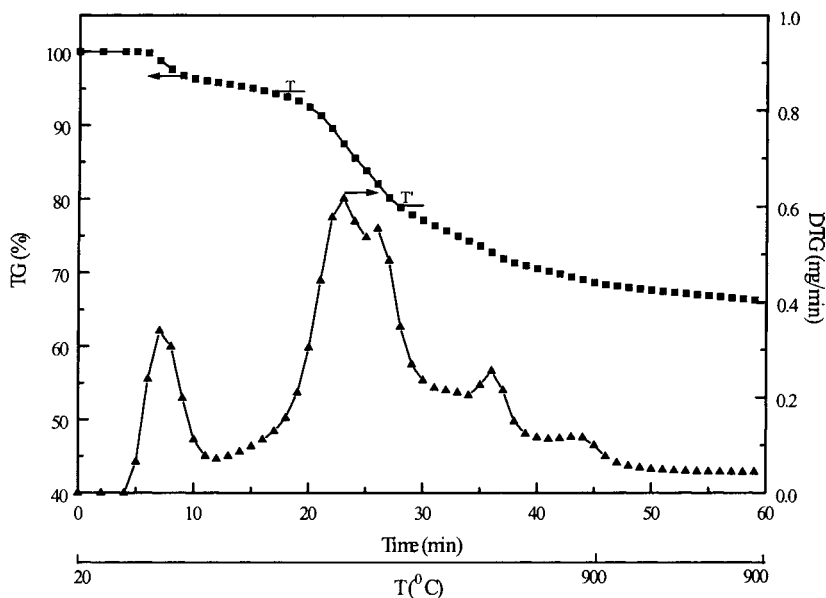


Fig. 1. TG and DTG curves of Tunçbilek lignite.

Maximum pyrolysis rate peak was observed at a temperature of 465°C, as 0.6165 mg/min for Tunçbilek lignite (Fig. 1). In addition, the volatile matter yield amounted to 39% of the total in the range 401–591°C for linear segment T–T’ of the TG curve.

As seen from Fig. 2, in the pyrolysis of Denizli peat, the volatile matter yield achieved ≈45.5% of the total from 265°C to 446°C, for the linear segment P–P’. The total volatile matter content of the peat was also found as 77% in the temperature range 265–900°C from the

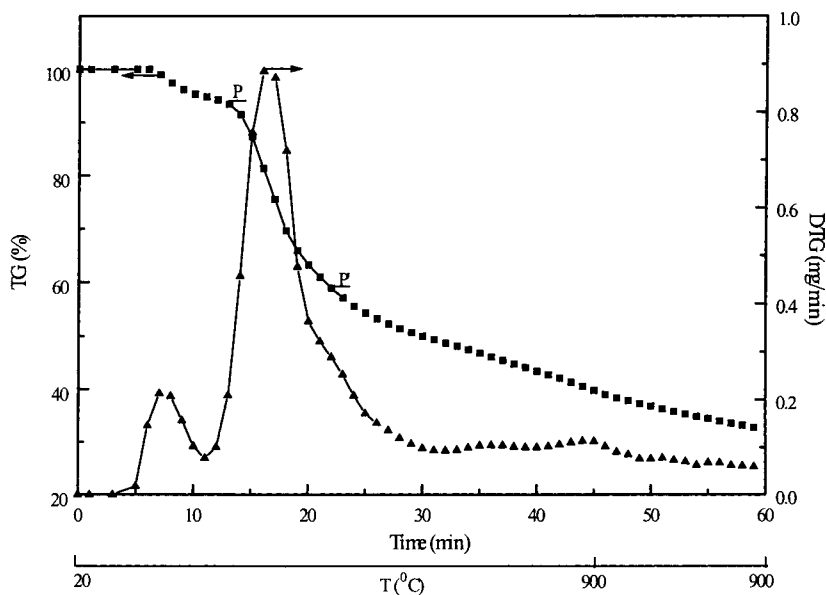


Fig. 2. TG and DTG curves of Denizli peat.

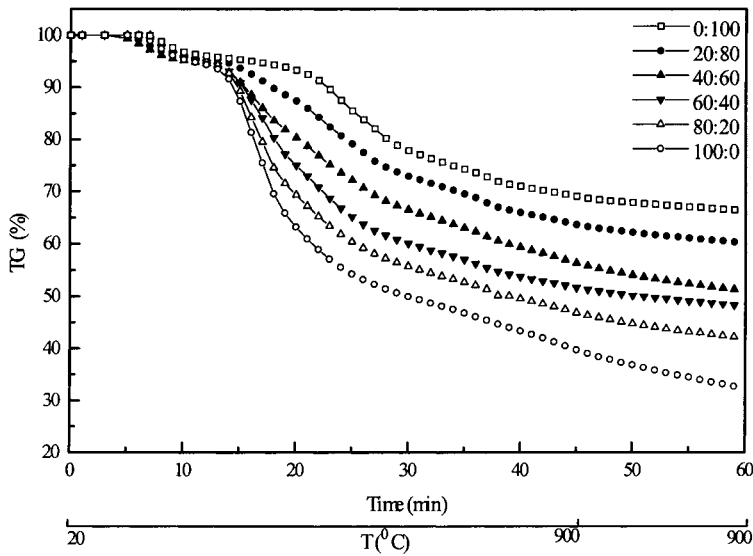


Fig. 3. TG curves of blends with different blending ratios of Denizli peat to Tunçbilek lignite.

same curve. The pyrolysis rate reached a maximum as 0.8844 mg/min.

3.2. Blends

Blends made of Denizli peat and Tunçbilek lignite were studied under the same pyrolysis conditions.

Blending ratios of Denizli peat to Tunçbilek lignite of 20:80, 40:60, 60:40 and 80:20 were performed. The TG and DTG curves of the blends are shown in Figs. 3 and 4, respectively.

It can be observed from Fig. 4 that the height of the DTG peaks gradually increase with increasing amount of peat in the blends. The change of the maximum

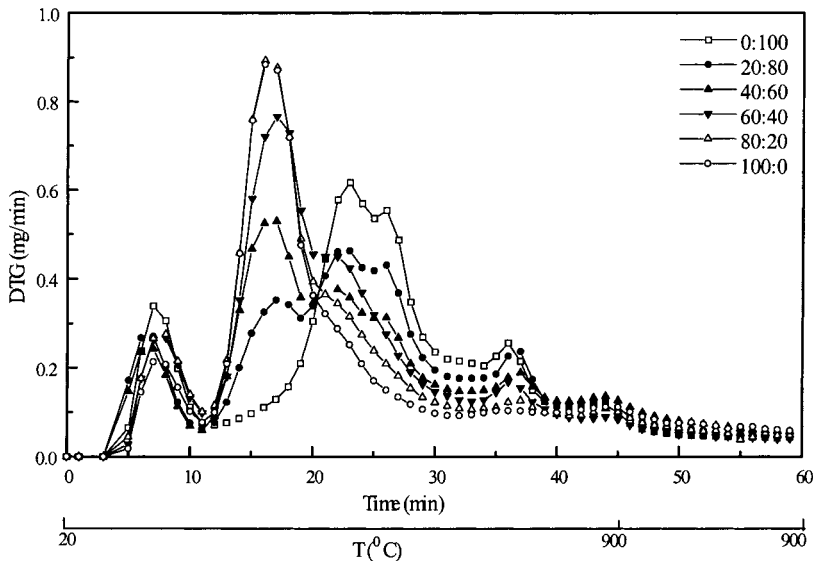


Fig. 4. DTG curves of blends with different blending ratios of Denizli peat to Tunçbilek lignite.

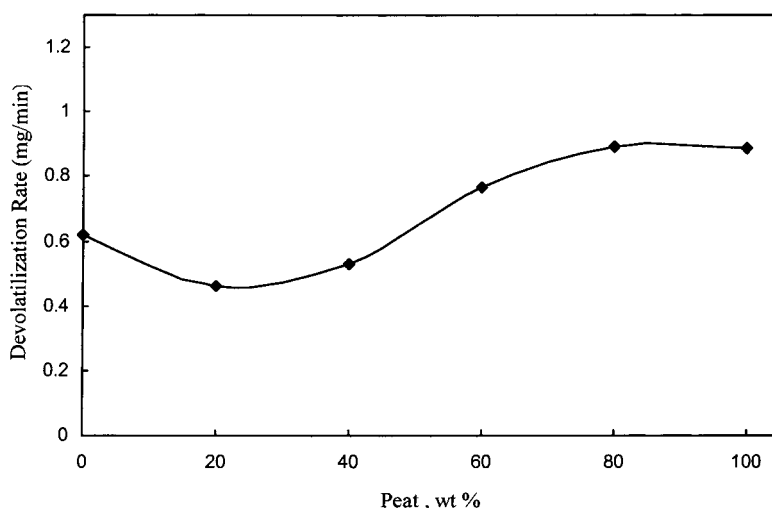


Fig. 5. Change of devolatilization rate with peat content of blends.

devolatilization rate with the blending proportion is shown in Fig. 5. A decrease in the values of the maximum devolatilization rate for the blending ratios of peat to lignite of 20:80 and 40:60 is observed when compared with the corresponding value obtained for the Tunçbilek lignite. The maximum rate was found for Denizli peat. Thus it is considered that the basic role of peat in blend is to supply large quantities of volatile matter per minute. The volatile matter yield achieved in these conditions is approximately in

accordance with the standard analysis of the peat (Table 1).

The main characterization point in the TG/DTG thermogram is the peak temperature (T_m), where the rate of weight loss is at maximum. The change of maximum temperature of devolatilization rate with the peat weight percentage of the blends is shown in Fig. 6. The maximum peak temperature of the blend with the ratio of peat to lignite of 20:80 is slightly higher than that of the lignite. A sharp decrease in the

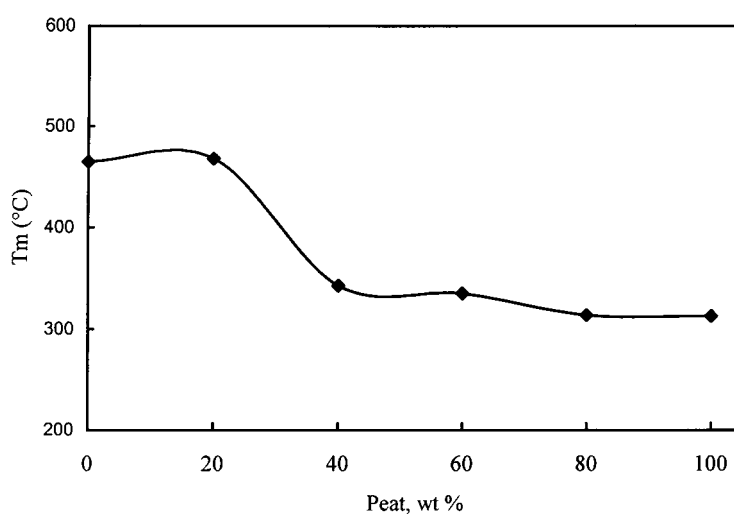


Fig. 6. Change of temperature of maximum devolatilization rate with peat content of blends.

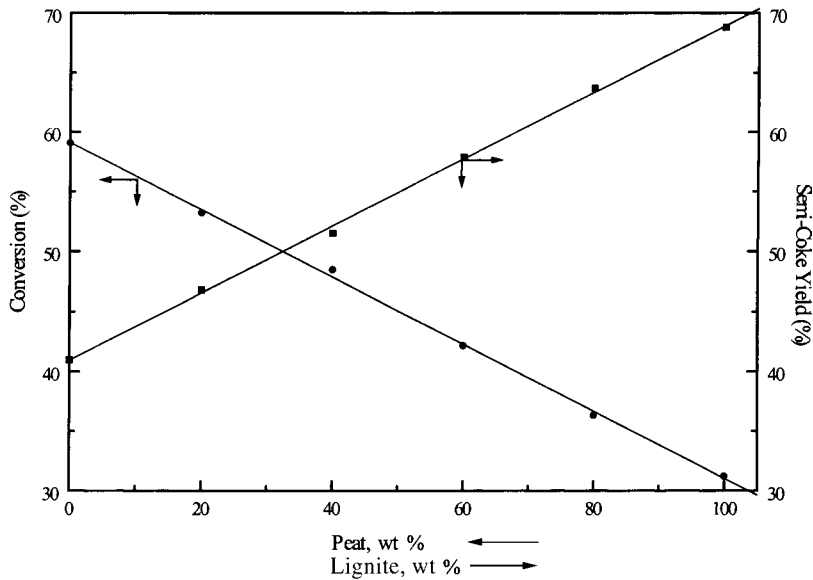


Fig. 7. Changes of semi-coke yields and conversion percentages with peat content of blends.

T_m values is observed for the higher weight percentages of the peat in blends.

Semi-coke yields and total conversion values of the blends were calculated based on the weight of the moisture-free blends fed to the system. Fig. 7 shows the change of semi-coke yields and total conversion values with the peat weight percentage of the blends. Although an increase in the conversion with increasing percentage of peat in blends was observed, semi-coke yields were decreased.

3.3. Kinetic model

Since it is virtually impossible to identify all elementary reactions which occur when coal is thermally decomposed, most reported kinetic models are based on either the decomposable weight of coal or the amount of gaseous product [14].

The proposed pyrolysis model in this study is

$$-\frac{dW}{dt} = k_0 e^{-E/RT} W^n, \quad (1)$$

where w is the weight of coal at any time, t (mg), k_0 the frequency factor ($[mg^{-(n-1)}/min]$), E the activation energy (kJ/mol), T the temperature (K), n the order of reaction, and t is the time (min).

In Eq. (1), E and n are the apparent activation energy and the total order of the whole pyrolysis process, respectively.

The logarithmic expression of Eq. (1) yields

$$\ln\left(-\frac{dw}{dt}\right) = \ln k_0 - \frac{E}{RT} + n \ln w. \quad (2)$$

In order to determine the pyrolysis kinetics of the individual feedstocks and their blends Eq. (2) was applied to the TG and DTG data. Assuming first-order kinetics ($n=1$), kinetic constants k_0 , E and square correlation coefficients (R^2) were determined from the multiple linear regression analysis and given in Table 2. An increase was observed

Table 2
Changes of kinetic parameters with the blending ratio of peat to Tunçbilek lignite

| Peat/lignite | k_0 (1/min) | E (kJ/mol) | R^2 |
|--------------|---------------|--------------|-------|
| 0:100 | 13 | 14.62 | 0.987 |
| 20:80 | 25 | 36.72 | 0.986 |
| 40:60 | 665 | 49.07 | 0.982 |
| 60:40 | 1654 | 51.33 | 0.990 |
| 80:20 | 5424 | 55.17 | 0.983 |
| 100:0 | 17854 | 59.64 | 0.981 |

in the frequency factor and activation energy values as the weight percentage of peat in blends increased.

4. Conclusion

On heating two different kinds of feedstock – Denizli peat (DP) and Tunbilek lignite (TUL) – from 25°C to 900°C at 20°C/min under an argon atmosphere, the following conclusions are derived: pyrolysis rate: DP>TUL; pyrolysis temperature (of start of pyrolysis): DP<TUL.

When a blend in any proportion of peat to lignite was pyrolyzed, an increase in maximum devolatilization rate and a decrease in devolatilization rate peak temperature (T_m) with the increase in peat content of the sample was observed for the blending ratio over 40:60.

A first-order reaction model was proposed to describe the main pyrolysis processes for both the individual feedstocks and their blends and activation energies and frequency factors were determined. Activation energy and frequency factor values for the proposed reaction model both increased with increase in the ratio of peat to lignite in blends. The changes in the values of these kinetic parameters might be due to the higher volatile matter content of the peat than lignite.

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