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Pyrolysis by thermogravimetric analysis of blends of peat with coals of different characteristics and biomass

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Abstract

In this study, an investigation was carried out into the thermal behaviours of peat, reed, lignite, bituminous coal and blends of these with peat. The blends were prepared in 20:80, 40:60, 60:40, 80:20. The samples were pyrolysed in a TG analyzer in a nitrogen atmosphere (50 mL/min) at temperatures ranging from 25 to 900 °C. Using TG/DTG graphs, variations were investigated, which occurred in reaction intervals, percent of weight loss, peak temperatures and maximum devolatilization rate. The activation energy (E) and pre-exponential constant (A) were calculated using the Arrhenius type kinetic model.

Keywords: Peat; Reed; Lignite; Bituminous coal; Pyrolysis; TGA; Kinetic analysis

1. Introduction

Coal is one of the most widely mined substances and is either used as a fuel directly or heated into secondary fuels. Therefore, the thermal properties of coal is of utmost importance to its use. The thermal properties determine the behaviours of coal in such processes as its combustion, gasification, pyrolysis and liquefaction (Mackenzie, 1970). Pyrolysis consists of a very complex reactions during which both chemical (endothermic and exothermic reactions like bond breaking, recombination) and physical (softening, resolidification) changes occur due to thermal effects (Tromp *et al.*, 1989). Pyrolysis by thermogravimetric analysis is an analytical method to determine the decomposition rate of reactions resulting from thermal effects and the kinetic parameters of these reactions (Shafizadeh and McGinnis, 1971). The kinetic analysis in the thermal decomposition is the most important tool in the study of the complex pyrolysis mechanism (Caballero *et al.*, 1997). In several publications it has been reported that weight loss occurs in relation to a constant increase in temperature and kinetic analysis is used in thermal analysis processes, such as pyrolysis of coal, biomass or blends of these (Biagini *et al.*, 2002; Cozzani *et al.*, 1995; Güldoğan *et al.*, 1999; Helsen and Van den Bulck, 2000; Jones *et al.*, 2005; Kastanaki *et al.*, 2002; Klose and Stuke, 1993; Koufopanos *et al.*, 1989; Meesri and Moghtaderi, 2002; Nassar, 1999; Pan *et al.*, 1996; Raveendran *et al.*, 1996; Vamvuka *et al.*, 2003, 2006; Vuthaluru, 2004a).

In this study, the pyrolytic behaviours of peat, reed, lignite and bituminous coal were investigated by means of thermogravimetric analyzer. Moreover, peat was blended with reed, lignite and bituminous coal in various proportions and the pyrolytic behaviours of the blends were also investigated. The kinetic parameters of all the samples were calculated using the Arrhenius kinetic model.

2. Experimental

2.1. Materials

In this study, the Yeniçağa peat (P), reed (Phragmites australis) (R), the Mengen lignite (L) and the Zonguldak class A bituminous coal (B) with a high volatile matter content were used, which were obtained from the Western Black Sea region of Turkey. The samples were ground below 250 μm. The proximate and ultimate analyses which were carried out according to ASTM standards are given in Table 1. The ultimate analyses were performed with a Leco-CHN elemental analyzer and a Leco-S132 sulphur analyzer. The calorific value was determined by using a IKA-Calorimeter C4000.

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Table 1
Proximate and ultimate analyses of samples

Sample	P	R	L	B
Ash[a]	18.81	6.38	9.37	18.25
VM[a]	61.19	76.16	54.38	26.92
FC[a]	20.00	17.46	36.25	54.83
C[b]	54.14	48.61	66.79	82.87
H[b]	5.35	5.98	4.90	5.00
N[b]	2.45	1.61	1.99	1.57
S[b]	0.86	0.15	9.91	0.56
Mj/kg[a]	17.41	18.74	26.50	36.35

[a] Dry free basis.
[b] Dry ash free basis.

The peat sample was blended with reed, lignite and bituminous coal separately in the proportions of 80:20, 60:40, 40:60, 20:80.

2.2. Method

The thermogravimetric analyses were carried out by a PL 1500 TGA apparatus in a nitrogen atmosphere (50 mL/min) at a temperatures ranging from 25 to 900 °C. The heating rate was 10 °C/min and the initial sample weight was approximately 20 mg. The experiments were performed twice in order to determine whether they did be repeated or not. During the 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 samples were subjected to a computer-controlled temperature programme. The initial portion of the pyrolysis curves were used to estimate the apparent first-order pyrolysis kinetics (Kök and Pamir, 2000).

2.3. Kinetic calculation

In order to determine the kinetic parameters, a first-order Arrhenius kinetic model was applied (Kök and Pamir, 2000; Kök, 1997; Pan *et al.*, 1996). According to the Arrhenius model (Jaber and Probert, 2000; Kök, 1993);

$$\frac{dW}{dT} = kW_n \quad (k = Ae^{-E/RT})$$

We assume the first-order reaction,

$$\frac{dW}{dT} = Ae^{-E/RT}W$$

$$\frac{dW}{dT}\frac{1}{W} = Ae^{-E/RT}$$

$$\log\left(\frac{dW}{dT}\frac{1}{W}\right) = \log A - \frac{E}{2.303RT},$$

where dW/dt denotes the weight loss (%/min), A the Arrhenius constant (min^{-1}), E the activation energy (kJ/mol), T temperature (K), n reaction degree and R is the gas constant (8.314 kJ/mol). When a graph of $\log((dW/dT)(1/W))$ against $1/T$ is plotted based on this model, the curve of the line obtained equals $E/2.303RT$, whereby the activation energy and pre-exponential constant can be calculated.

3. Results and discussion

3.1. Pyrolysis

In this study, the pyrolytic behaviours and kinetic parameters of a given amount of the samples in a given size were investigated. Accordingly, the −250 μm samples (Vamvuka *et al.*, 2003) weighing about 20 mg (Güldoğan *et al.*, 1999) were subjected to a thermogravimetric analyses.

Fig. 1 gives weight loss in relation to temperature during the pyrolysis of the samples. The behaviours of the TG curves of the blended samples bear a resemblance to those of the TG curves of the individual samples in the blends (Moghtaderi *et al.*, 2004). In the pyrolysis of blends with reed, as the proportion of peat increases, so does the weight loss (Fig. 1i). In blends with lignite and bituminous coal, there is a decline in the weight loss with a decreasing peat proportion (Fig. 1ii and iii). This is attributable to the fact that the reed suffers a sudden

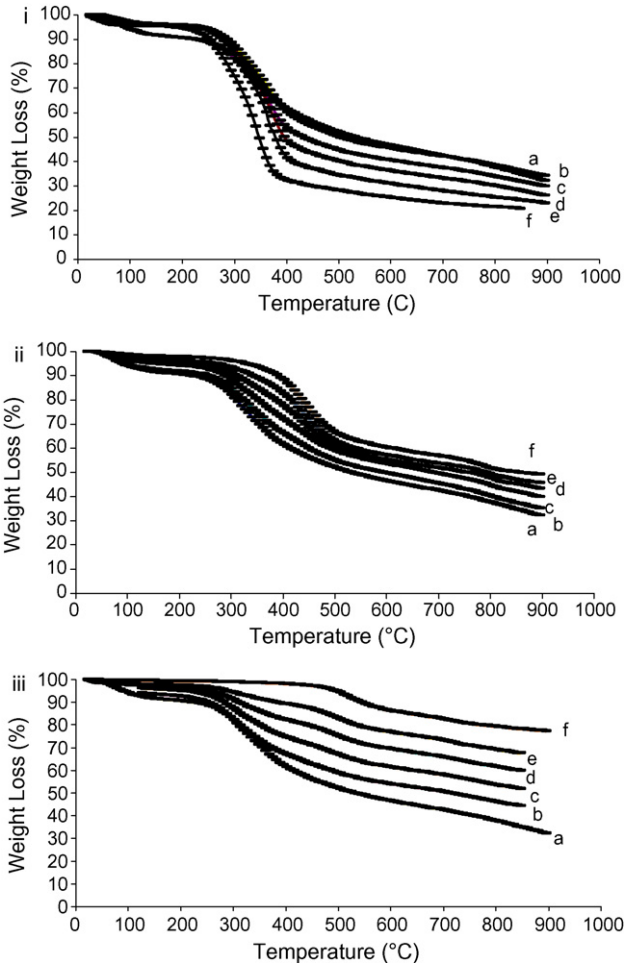

Fig. 1. TGA curves of samples. (i) (a) 100%P, (b) 80%P + 20%R, (c) 60%P + 40%R, (d) 40%P + 60%R, (e) 20%P + 80%R, (f) 100%R. (ii) (a) 100%P, (b) 80%P + 20%L, (c) 60%P + 40%L, (d) 40%P + 60%L, (e) 20%P + 80%L, (f) 100%L. (iii) (a) 100%P, (b) 80%P + 20%B, (c) 60%P + 40%B, (d) 40%P + 60%B, (e) 20%P + 80%B, (f) 100%B.