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THERMAL ANALYSIS OF BEYPAZARI LIGNITE

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Abstract

Beypazari lignite was investigated by differential scanning calorimetry (DSC), thermogravimetry (TG), high pressure thermogravimetry (HPTG) and combustion cell experiments. All the experiments were conducted at non-isothermal heating conditions with a heating rate of 10°C min^{-1}, in the temperature range of 20–700°C. DSC-TG data were analysed using an Arrhenius-type reaction model assuming a first-order reaction. For the HPTG data the Coats and Redfern equation was used for kinetic analysis. In the combustion cell experiments the Fassihi and Brigham approach was used in order to calculate kinetic data. Finally a comparison is made between the kinetic results.

Keywords: combustion, kinetics, lignite, thermal analysis

Introduction

Characterisation of fossil fuels and understanding of reactions involved during their pyrolysis and combustion by thermal analysis techniques (differential scanning calorimetry-DSC- and thermogravimetry-TG-) and their characterisation under pressurised conditions enables researchers to find optimum parameters and solutions to problems. Mahajan and Tomita [1] reported DSC curves for twelve coals of various ranks under helium atmosphere at 5.6 MPa pressure and up to 580°C. They concluded that the thermal effects during pyrolysis of coals ranging in rank from anthracite to bituminous coal were endothermic. The specific heat of the coals and the enthalpy changes characterising their thermal degradation were investigated by Elder and Harris [2]. They found that during pyrolysis, endothermic heat flow occurred from 300 to 550°C. Gold [3] demonstrated the occurrence of exothermic reactions associated with the production of volatile matter in or near the plastic region of coals studied. He concluded that the temperature and magnitude of the exothermic peak was strongly affected by the heating rate, sample mass and particle size. Rosenvald and Dubow [4] analysed the pyrolysis of bituminous coal samples by DSC and TG. They distinguished three regions of endothermic activity in the DSC experiments in an inert atmosphere. Butler and Soulard [5] determined the specific heat of both dried and original, untreated coals as a function of temperature and concluded that the specific heat of dried coals increased with increasing temperature. Smith and Neavel [6] reported TG results on coal combustion up to 900°C. He

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obtained four distinct regions of reactivity considering a first order reaction. Morgan and Robertson [7] pointed out that coal burning profiles obtained from thermogravimetric analysis depends critically upon experimental procedures and equipment design. Kök and Okandan [8–9] determined the effect of crude oil type and heating rate on combustion of lignite-crude oil mixtures using DSC and TG at atmospheric conditions. Their results indicate that the characteristic curve shape belonging to the combustion of Beypazari lignite was not changed by the addition of crude oil but that higher heating rate cause a shift of the reactions to higher temperatures. Haykiri *et al.* [10] applied DTA and TG techniques to characterise lignite, bituminous coal, anthracite and oil shales under nitrogen atmosphere. Mianowski and Radko [11) developed a method for the evaluation of the temperature range in order to calculate the kinetic parameters of coal pyrolysis. For coal samples of different rank, it is shown that pyrolysis in the temperature range 553–853 K is a first-order process with an activation of 78–151 kJ mol^{-1}. Collett and Rund [12] studied the thermogravimetric measurements of mass loss accompanying the pyrolysis of four pitches over two ranges of linear heating rates. The data for all samples were described by the multiple heating rate method and activation energy increased with increasing heating rate. Shah *et al.* [13] reported non-isothermal thermogravimetry (TG) and derivative thermogravimetry (DTG) studies on lignite and sub bituminous coal. The burning profiles of the samples showed a multi-peak configuration which is indicative for the heterogeneity of the organic matter. The volatile matter profiles of these samples are characterised by the rate of mass loss.

Experimental

In the first part of the experiments DuPont 9900 thermal analysis system with differential scanning calorimetry (DSC) and thermogravimetric analyser (TG/DTG) modules were used. In the second part, experiments were carried out using a Sartorious high pressure thermobalance (HPTG) which was constructed by modification of the high pressure micro balance. Finally a combustion cell was used to study the kinetics of the lignite sample. The sample studied was Beypazari lignite with a particle size <60 mesh and prepared according to ASTM standards at the beginning of the experiments. Properties of the Beypazari lignite are given in Table 1. DSC and TG experiments were conducted at five different heating rates in the temperature range of 20–600°C. The air flow rate was kept constant at 50 ml min^{-1} . In order to get an impression of the reproducibility, the experiments were performed twice. Prior to the experiments the DSC and TG equipments were calibrated for

Table 1 Properties of Beypazari lignite

Ash/%	Vol. Mat./%	Moisture/%	Fix. Carb./%	C/%	H/%	N/%
36.4	30.0	8.6	25.0	37.9	2.9	1.4

temperature readings using indium. All HPTG experiments were performed at a linear heating rate of 10°C min^{-1} over the temperature range of 25–600 °C with an air flow rate of 53 ml min^{-1} within the total pressure range of 100–300 psig. Prior to the experiments the HPTG instrument was calibrated for temperature readings and buoyancy effects. In order to assess the reproducibility, experiments were performed twice. Figure 1 represents the schematic diagram of a HPTG instrument. The design and operating conditions are given elsewhere [14]. Combustion cell experiments were performed using an experimental apparatus which includes a combustion cell (essentially a small differential reactor) equipped with a furnace, flow metering and pressure regulation, temperature measurement and control, and gas analysis devices. Before starting the experiments the O_2, CO and CO_2 analysers were calibrated by passing a mixture with oxygen free nitrogen gas through the analysers. The combustion cell was heated with a constant heating rate of 10°C min^{-1} up to a temperature of 750°C in each experiment. Figure 2 represents the schematic flow diagram of the experimental apparatus.

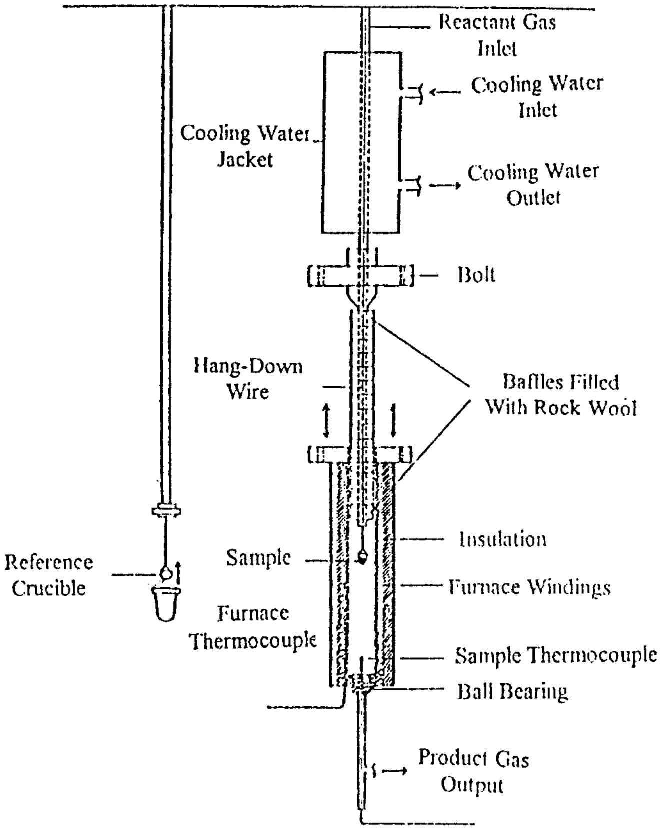

Fig. 1 Schematic diagram of the high pressure TG equipment

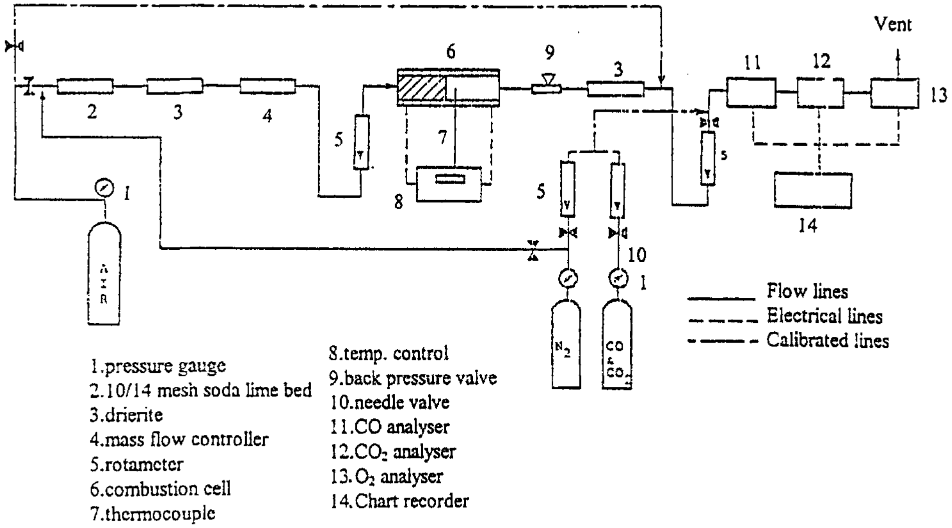

Fig. 2 Schematic diagram of the combustion cell equipment

Results and discussion

Theoretically, combustion of fuel starts whenever oxygen comes in contact with fuel. The combination of fuel, oxygen availability and temperature controls the nature of this reaction. The DSC curve of Beypazari lignite showed one main reactivity region. The heat flow rate recorded at different temperatures showed that the oxidation reaction started around 250°C and reached a maximum rate at 410°C (Fig. 3). The shoulder on the high-temperature side of the DSC curve was attrib-

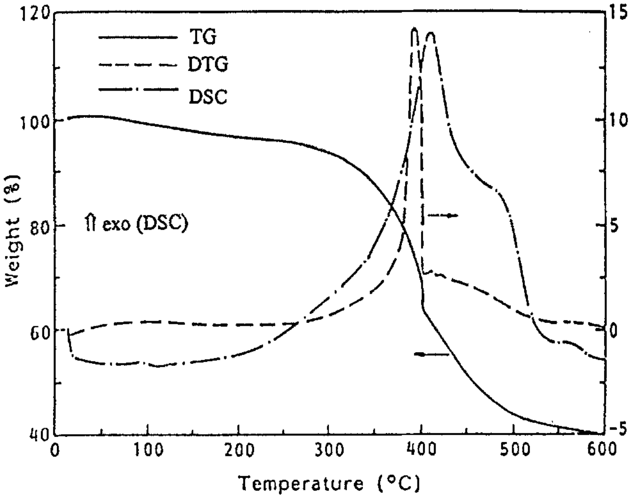

Fig. 3 DSC, TG/DTG curves of Beypazari lignite

uted to the possible swelling of the sample, resulting in an impermeable mass that reduced the oxygen accessibility. The TG/DTG curves (Fig. 3) of the lignite showed an identical shape. The maximum rate of mass loss occurred at 390°C, followed by another mass loss region which corresponded to the shoulder observed on the DSC curve. During this research, DSC and TG experiments were performed at heating rates of 5, 10, 15, 20 and 25°C min^{-1}. Higher heating rates resulted in higher reaction temperatures, and higher DSC signal values (Table 2). Distinguished peaks in the DSC curves shifted to higher temperatures with an increase in heating rate (Fig. 4). The effect of the heating rate on the kinetic parameters of the lignite sample was also investigated [8–9] and similar activation energies were obtained at each run (Table 3).

Table 2 Heat flow rates (mcal s^{-1}) and, peak temperatures (°C) and total heat combustion (J g^{-1}) of the samples at different heating rates

5°C min^{-1}	10°C min^{-1}	15°C min^{-1}	20°C min^{-1}	25°C min^{-1}
10.9	26.67	39.80	48.14	49.94
387	409	422	432	437
11050	11240	12800	13150	140250

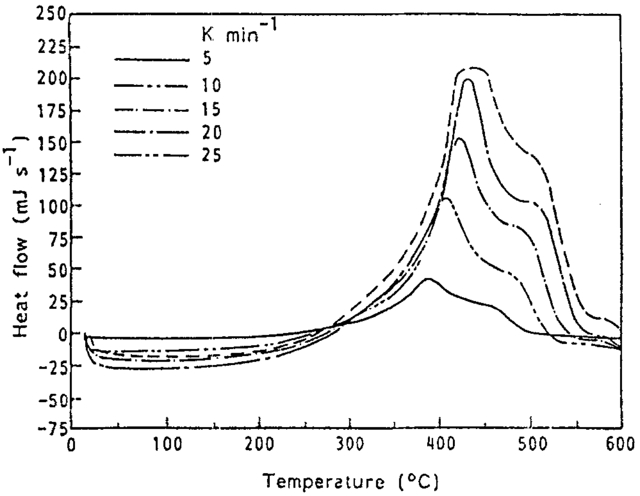

Fig. 4 DSC curves of Beypazari lignite at different heating rates

Table 3 Activation energies (kJ mol^{-1}) of Beypazari lignite at different rates, measured with DSC

5°C min^{-1}	10°C min^{-1}	15°C min^{-1}	20°C min^{-1}	25°C min^{-1}
68	69	66	69	65

Another method developed by ASTM committee [15] for chemical reactions provides a means for determining activation energies using DSC data. Determination of kinetic parameters by the peak temperature from DSC experiments requires very precise measurement of reaction peak temperatures as a function of linear programmed heating rates. Activation energy of Beypazari lignite was calculated as 68 kJ mol^{-1}.

Thermogravimetric (TG/DTG) data were analysed according to an Arrhenius type kinetic model [16],

$$[\mathrm{d}x/\mathrm{d}t(1/x)] = A\exp(-E/RT) \qquad (1)$$

where; $\mathrm{d}x/\mathrm{d}t$ is the rate of mass change of the reacting material, A is the Arrhenius constant, E is the activation energy (kJ mol^{-1}), T is the temperature (K) and n is the reaction order.

From the previous studies [8, 9] it was found that combustion of lignite can be accepted as a first order reaction. Therefore the data reported here were obtained by taking $n=1$. From the above expression, activation energy of the lignite was found 66 kJ mol^{-1} .

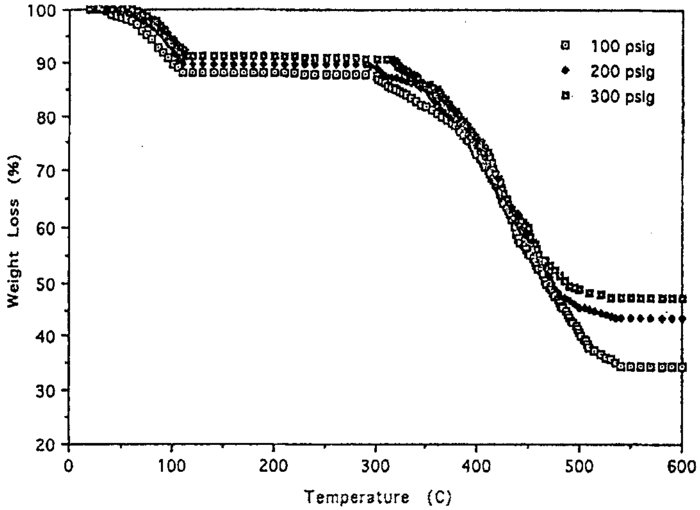

Fig. 5 HPTG curves of Betpazari lignite at different pressures

In the second part of the research, high pressure TG experiments were carried out to explore the effect of total pressure (100–200 and 300 psig) on the combustion behaviour and kinetics of the lignite sample (Fig. 5). In an oxidative environment one reaction region was identified in all experiments. The reaction intervals shift higher temperature regions as the total pressure was increased. The amount of sample left at the end of the reaction was also increased as the pressure was increased. The reaction intervals and the amount of sample left at the end of the reactions at different pressures are given in Table 4.

Table 4 Reaction intervals (°C) and amount of sample left (% wt) at the end of the reactions, measured by HPTG

	100 psig	200 psig	300 psig
Reaction interval	300–535	305–540	310–545
Sample left	34.5	43.5	47.0

In this research solid phase thermal decomposition is described by the following rate expression [17].

$$dx/dt=k(1-x)^n \qquad (2)$$

$$x=(W_0-W_t)/(W_0-W_f) \qquad (3)$$

$$k=Ae^{-E/RT} \qquad (4)$$

where; k: rate constant, n: order of reaction, W_0: initial sample mass, W_t: sample mass at time t, W_f final mass, A: Arrhenius constant, E: activation energy, R: gas constant, T: absolute temperature.

For a linear heating rate, $b=dT/dt$, and by combining above equations, rearranging, integrating and taking the natural logarithm and assuming $n=1$, we obtain,

$$\ln[-\ln(1-x)/T^2)=\ln(AR/bE)[1-(2RT/E)]-(E/R)1/T \qquad (5)$$

A plot of $\ln[-\ln(1-x)T^2]$ *vs.* $1/T$ should result in a straight line of slope $=E/R$. Typical plots to obtain apparent activation energies at different pressures are shown in Fig. 6 whereas activation energy values obtained at each total pressure is given in Table 5. No effect of pressure was observed on the kinetic parameters.

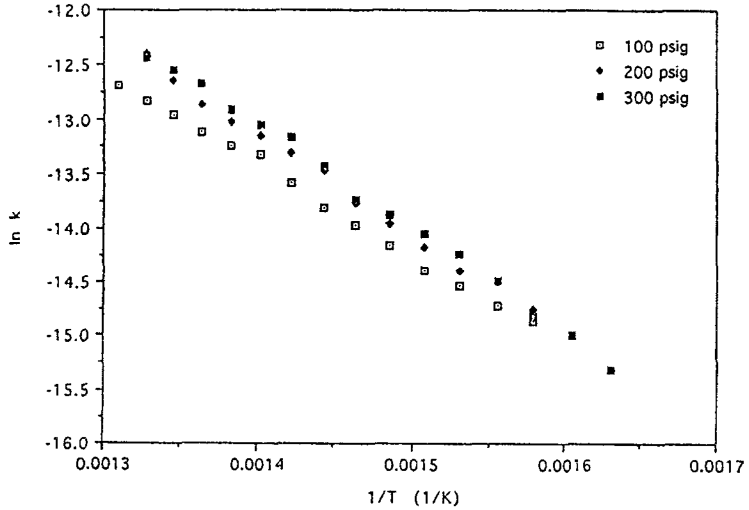

Fig. 6 Arrhenius plot of Beypazari lignite at different pressures

Table 5 Activation energies (kJ mol^{-1}) of Beypazari lignite at different pressures, measured by HPTG

100 psig	200 psig	300 psig
68.2	69.4	69.8

In the combustion cell experiments, the initial objective was to analyse the gases produced from the combustion reaction whilst heating the sample to a temperature of 750°C. As the temperature was increased to 750°C at a heating rate of 10°C min^{-1}, carbon dioxide, carbon monoxide, and oxygen gas were continuously analysed and temperatures were recorded. At low temperatures, some oxygen is consumed to produce carbon oxides but the carbon dioxide and carbon monoxide produced are less than corresponds to consumption. This indicates that some oxygen is consumed in other reactions. But at high temperatures the amount of consumed oxygen was nearly equal to the carbon dioxide and carbon monoxide produced. A kinetic model developed and adapted to reaction kinetics studies by Fassihi and Brigham [18] was used in the determination of kinetic parameters. In this model, the temperature is linearly increased with time and the relative reaction rates can be calculated by using the oxygen consumption values and their change with time and temperature. A computer program was used [19] to calculate the relative reaction rate. In order to determine activation energy from the relative reaction rate, experimental points are fitted to a straight line and the points that show extensive departure are discarded. From this procedure the activation energy of the Beypazari lignite was determined as 72 kJ mol^{-1}.

Conclusions

The DSC and TG/DTG curves of Beypazari lignite showed one main reactivity region. The heat flow rate recorded at different temperatures showed that oxidation reaction started around 250°C and reached a maximum rate at 410°C. Higher heating rates resulted in higher reaction temperatures, and heat of reactions. Distinguishing peaks in the DSC curves shifted to higher temperatures with an increase in heating rate. In HPTG experiments, one reaction region was identified in all experiments. Reaction intervals are shifted from low to higher temperature regions as the total pressure was increased. In combustion cell experiments, some oxygen is consumed to produce carbon oxides but the carbon dioxide and carbon monoxide produced were lower than the oxygen consumed at low temperatures which indicates that some oxygen is consumed in other reactions. But at high temperatures the amount of consumed oxygen was nearly equal to carbon dioxide and carbon monoxide produced. The activation energies obtained from the different methods were identical and considered as first order mechanism.

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