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PYROLYSIS KINETICS AND CHEMICAL COMPOSITION OF HAZRO COAL ACCORDING TO THE PARTICLE SIZE

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The relationship between particle size and chemical composition of Hazro coal (origin: SE Anatolia, Turkey) has been examined by elemental analysis and by thermogravimetric pyrolysis.

The chemical composition of the coal was determined by grinding sample particles physically and separating according to their size in mm by sieving. Particle size distribution of the coal and chemical composition of these fractions were given.

The coal has been non-isothermally pyrolysed in a thermogravimetric analyser to determine the kinetic factors. Thermal gravimetric (TG/DTG) experiments were performed from ambient temperature to 800°C under a nitrogen atmosphere at heating rate 10 K min^{-1} with five different particle size ranges. Kinetic parameters of the samples were determined using a Coats and Redfern kinetic model, assuming a first-order reaction. Depending on the particle size of the coal samples, the mean activation energy values varied between 49.1 and 84.6 kJ mol^{-1}. The results discussed indicate that activation energies increase as the particle size decreases.

Keywords: *coal, elemental analysis, kinetic analysis, particle size, pyrolysis, thermogravimetry*

Introduction

Coal is an extraordinarily complex and heterogeneous material whose physical and chemical properties are difficult to determine. Turkey possesses substantial coal reserves [1]. Data on the chemical composition and structure of coal samples are still limited, despite the need for such data on economic and environmental grounds. New and effective analytical methods are thus necessary for the more efficient utilisation of such coal samples [2–4].

The combustion and pyrolysis processes taking place in fossil fuels have been studied [5–24]. Pyrolysis is the initial step in most coal-conversion processes, such as combustion, gasification and liquefaction, and has a significant influence on all subsequent stages.

Accurate descriptions of coal pyrolysis are helpful in the effective utilisation of coal and also important in the development of new pollution-control strategies [9–12]. Pyrolysis products depend on various parameters such as the type of coal, particle size of the sample, temperature, heating rate, time, pressure, sweep-gas velocity, and gas residence time [7–15, 25].

In recent years, the application of thermogravimetry (TG), differential scanning calorimetry (DSC) and derivative thermogravimetry (DTG) to study the combustion and pyrolysis behaviour of fossil fuels has gained widening acceptance among research workers, because of the importance of the resulting data for both industry and for the economy [13–31].

This paper determines the kinetic parameters for the pyrolysis of Hazro coal. Coal particle sizes were examined to determine the frequency factors and elemental composition.

Experimental

Hazro coal from the Southeast Anatolia region of Turkey was used in this study. The coal sample was prepared according to ASTM standards [7, 10, 19, 32, 33]. The coal sample was dried in a vacuum desiccators and then crushed by means of a jaw crusher (Retsch BB 1/A), then ground in a rotor-beater mill (Retsch SRZ). The resulting material was then divided into representative sub-samples using an analytic sample divider (Retsch PT2). Test sieving was employed for particle-size analysis, using a Retsch 3B test-sieving device fitted with Tyler-series sieves (0.053–3.36 mm). The sieve analysis of the coal sample is presented in Table 1. C, H, N and S analyses were performed using a Carlo Erba element-analysis instrument (model EA 1108). The technique used for the determination of C, H, N and S is based on the quantitative 'Dynamic Flash Combustion' method [32, 33]; the technical specifications of the EA 1108 elemental analyser are given elsewhere

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Table 1 Results of Hazro coal samples sieve test

Screen size/ mm	Mass remaining/ %	Screen oversize/ mass%	Screen undersize/ mass%
–3.360+0.600	7.0	7.0	93.0
–0.600+0.250	16.0	23.0	77.0
–0.250+0.125	27.0	50.0	50.0
–0.125+0.071	26.0	76.0	24.0
–0.071+0.053	24.0	89.0	11.0

[32]. The instrument was calibrated with the analysis of standard compounds using K-factors calculation [33]. The heating value, ash content, volatile matter, moisture and fixed carbon of the coal as proximate analysis were determined according to ASTM methods and are given in Table 2. The pyrolysis experiments were carried out by non-isothermal thermogravimetry using a Schimadzu TGA-50 Analyser. Thermal gravimetric experimental procedure involves placing the sample (max. amount 20 mg) into a platinum crucible and then heating from ambient to 800°C at a linear heating rate of 10 K min^{-1} and with a nitrogen flow rate of 15 mL min^{-1}. Prior to experiments, mass and temperature modules of the analyser were calibrated to obtain dependable and reproducible mass and temperature data before the experiments. The mass losses occurring in correspondence to the temperature rises were continuously recorded with a computer working in coordination with the furnace and the control unit of the analyser, in order to collect the data required to determine the pyrolysis characteristics and kinetics of the samples.

Table 2 Proximate, element and sulphur analysis of Hazro coal

Parameter	Coal
Proximate analysis/mass%	
Ash	18.310
Volatile matter	47.800
Fixed carbon	32.353
Moisture	1.537
Heating value/kcal kg^{-1}	6964.848
Elemental analysis/mass%	
Carbon	64.284
Nitrogen	1.020
Hydrogen	4.708
Sulphur	7.740
Sulphur distribution/mass%	
Pyritic	5.234
Sulphate	0.095
Organic	2.211

Results and discussion

Coal is a complex organic polymer consisting of aromatic clusters of several fused rings strung together by asserted hydrocarbon and heteroatom (O, N and S) linkages [1, 19]. The heterogeneous nature of coal and the complexity of the process have made it very difficult to perform unambiguous experiments on pyrolysis [10]. Heating causes the structure to decompose, the weaker bonds rupturing at lower temperatures and the stronger ones at higher temperatures. Fragments that are volatile tend to escape from the particle. Some of the fragments are highly reactive free radicals subject to a variety of secondary reactions such as cracking. Repolymerization products that are obtained through carbonization depend on coal composition, carbonization temperature and the heating rate [11]. On the basis of the relative amount of volatiles released during the various stages of pyrolysis it is possible to make a classification of coals that reflects rank and oxidation degree. The higher the rank of coal, the higher the temperature at which volatile matter is released, the shape of the thermogravimetric curve being a characteristic of rank [20]. There are a number of possible approaches for modelling the complex devolatilization process. The simplest are empirical and employ global kinetics, where the Coats and Redfern expression is used to correlate rates of mass loss with temperature. The single-step models postulate that the devolatilization process can be represented by the reaction

$$\text{Coal} \rightarrow x(\text{volatiles}) + (1-x)\ (\text{char});$$

where x is the volatile fraction [17].

Table 3 shows the elemental composition as a function of particle size in the studied coal sample, and indicates that the percentage of carbon increases as the percentage of sulphur decreases generally. The data given in Table 3 are of for total sulphur, and they are most likely biased by the liberation of pyrite during the grinding. Only physically bound water and small amount of CO and CO_2 were evolved by temperatures lower than 300°C. Water, which evolved above 300°C,

Table 3 Elemental composition as a function of particle size in Hazro coal

Particle size/mm	Hazro coal/%			
	C	S	H	N
–3.360+0.600	66.096	10.341	5.056	1.084
–0.600+0.250	67.062	7.659	5.003	1.063
–0.250+0.125	68.295	5.651	4.910	1.052
–0.125+0.071	64.959	7.369	4.697	1.007
–0.071+0.053	64.024	7.742	4.562	0.917

is produced by decomposition of various oxygen-containing groups, mainly OH-groups, leading to the formation of this pyrolysis water in a rather broad temperature range. Another source of water in this temperature range is the release of the crystal water from the inorganic components. 300–800°C is the temperature range in which mainly pyrolysis occurs. In addition to H_2O, CO, CO_2, aliphatic and aromatic volatiles were released at this temperature range, indicating the breaking of the aliphatic bridges and chains [34, 35]. The TG/DTG curves of all the size fractions show slight differences in peak temperatures and residue-left percentage (Table 4). As the peak temperature decreased the residue increased slightly. This can be explained when the particle size decreases, since gas reaches every coal particle more easily, volatilisation continues until relatively higher temperatures, and much more mass loss is observed at higher temperatures.

Table 4 Peak temperatures and residues of different fractions

Particle size/mm	Peak temp./°C	Residue left/%
–3.360+0.600	469.1	31.24
–0.600+0.250	458.5	34.33
–0.250+0.125	459.0	33.15
–0.125+0.071	468.1	31.17
–0.071+0.053	468.8	28.90

A first-order reaction model was proposed to describe the main pyrolysis processes for both the individual feedstock and their blends, and activation energies and frequency factors were determined.

Modelling of a reaction for combustion process of coal is extremely complicated because several components are oxidized simultaneously. In the present work, TG data were analyzed according to a Coats and Redfern kinetic model [8, 30, 36–38]. The calculation of the kinetic data is based on the formal kinetic equation

$$d\alpha/dt=k\alpha n$$

where α the amount of sample undergoing the reaction, n is the order of reaction and k is the specific rate constant.

Coats and Redfern developed an integral method, which can be applied to TG data, assuming the order of reactions. The correct order is presumed to lead to the best linear plot, from which the activation energy is determined. The final form of the equation, which is used for the analysis, takes the form

$$\log[-\log(1-\alpha)/T^2]=\log AR/\beta E[1-2RT/E]- -E/2.303RT \text{ for } n=1;$$

where β is the heating rate.

By plotting the appropriate left-hand side of the equations *vs*. $1/T$, the slope equals $-E/2.303R$. The activation energy (E), Arrhenius constant (A) and reaction rate constant (k) can be calculated from these equations [37]. The straight-line plots for coal samples are given in Figs 1–5 and calculated reaction parameters are cited in Table 5. An increase is observed in activation-energy values as the particle size decreases.

From the results obtained in this work, it can be concluded that the approach of a single reaction, used in pyrolysis kinetic calculations, may be useful in the comparison of different samples or different pyrolysis processes.

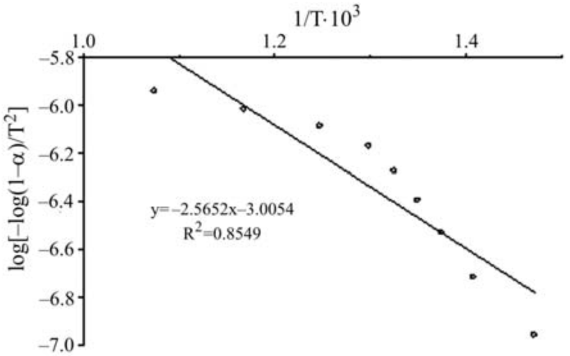

Fig. 1 Coats and Redfern plots of Hazro coal for different particle sizes (–3.36+0.60 mm) for reaction order of 1

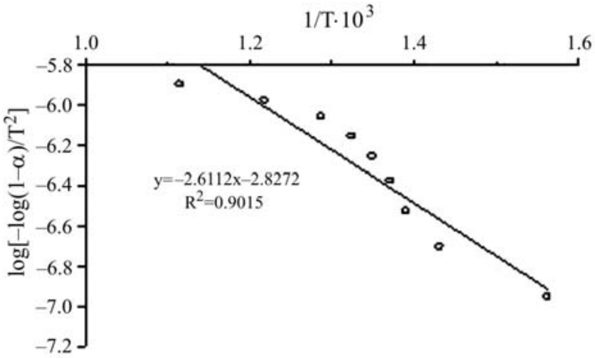

Fig. 2 Coats and Redfern plots of Hazro coal for different particle sizes (–0.60+0.25 mm) for reaction order of 1

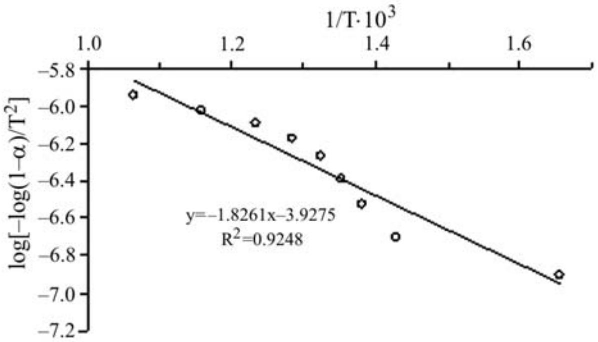

Fig. 3 Coats and Redfern plots of Hazro coal for different particle sizes (–0.25+0.125 mm) for reaction order of 1

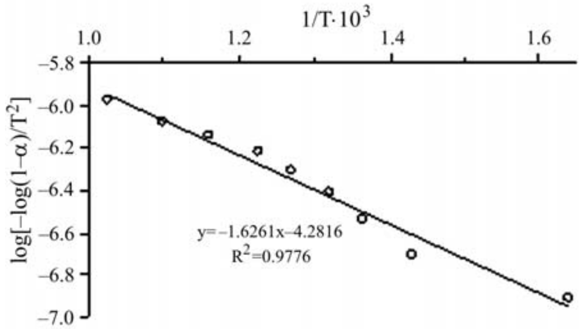

Fig. 4 Coats and Redfern plots of Hazro coal for different particle sizes (–0.125+0.071 mm) for reaction order of 1

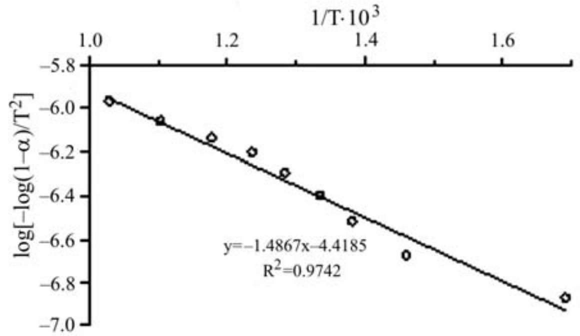

Fig. 5 Coats and Redfern plots of Hazro coal for different particle sizes (–0.071+0.053 mm) for reaction order of 1

Table 5 Reaction parameters of the coal samples

Particle size/mm	E/kJ mol^{-1}	A/L min^{-1}	$k\cdot10^{-3}$/min^{-1}
–3.360+0.600	49.116	5.719	1.999
–0.600+0.250	54.133	14.685	2.005
–0.250+0.125	75.200	1.863	8.034
–0.125+0.071	81.980	0.898	1.522
–0.071+0.053	84.602	0.684	7.558

E – activation energy, A – Arrhenius constant and $k\cdot10^{-3}$ – reaction rate constant

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