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Particle size effect on the oxidation mechanism of lignites

Mustafa Versan Kök*

Department of Petroleum and Natural Gas Engineering, Middle East Technical University, 06531, Ankara, Turkey

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Abstract

In this research, effect of particle size on the oxidation mechanisms of *Çayirhan, Tunçbilek* and *Soma* lignites are studied. Non-isothermal thermogravimetry and derivative thermogravimetry (TG/DTG) experiments were carried out for 12 different size fractions. Data obtained from TG/DTG experiments are converted into dimensionless time (instantaneous size/original size) versus dimensionless time (time/burn-out time) to show the progress of oxidation mechanisms of lignites. It was found that lignites show linear behaviour at elevated temperatures, which justifies the assumption that chemical reaction is the controlling step. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Lignite; Combustion; Particle size; Oxidation mechanism

1. Introduction

Coal is physically heterogeneous and chemically complex mixture of organic and inorganic species, which undergoes appreciable physico-chemical changes when heat is treated. The main studies of coal using thermal analysis techniques include characterisation of high-pressure application to coal hydrogenation, catalytic effects due to inorganic substances, combustion, pyrolysis and kinetic analysis. In the selection of coals for combustion it is useful to have knowledge of their combustion characteristics. Ignition and combustion of coal by mechanical stokers, fluidised beds or gasifiers is accompanied by weight loss, thermal decomposition, diffusion and heat transfer. These, in turn, are influenced by the nature of the coal, particle size, density and porosity, all of which govern the thermal processes occurring in the coal. Thermal analysis plays an important role in the investigation of useful mineral substances. Their application to the study of coals and its products has increased considerably in the last two decades. TG/DTG and DSC are the methods widely used in characterization of fossil fuels undergoing combustion or pyrolysis. Gold [1] demonstrated the occurrence of exothermic reactions associated with the production of volatile matter in or near the plastic region of coal studied. He concluded that the temperature and the magnitude of the exothermic peak were strongly affected by the heating rate, sample mass and particle size. Morgan et al. [2] pointed out that coal-burning profiles obtained from TG/DTG analysis depends on coal properties and particle size. Morris [3] carried out pyrolysis experiments in the temperature range of 20–900°C for different particle sizes and the established empirical's for the evaluation rates of hydrogen, carbon monoxide and methane as a function of particle size and instantaneous temperature. Jayaweera et al.

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*Tel.: +90-312-210-48-91; fax: +90-312-210-12-71
E-mail address: kok@rorqual.cc.metu.edu.tr (M.V. Kök)

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[4] studied the effect of particle size on the percentage weight loss of a low quality bituminous coal by thermal analysis techniques. It was found that the method of sieving used to prepare the samples of different particle size has significant effect on the results. Shah et al. [5] studied the combustion properties of different size coal samples. The results revealed the effect of reduction in particle size and burnout temperature, and yields of carbon monoxide and carbon dioxide as a function of particle size at a burnout temperature before decomposition of the carbonates in the mineral matter.

The objective of this research was to check whether chemical reaction is the controlling mechanism in lignite burning according to the unreacted core model for shrinking spherical particles. For this purpose data obtained from TG/DTG experiments are converted into dimensionless time (instantaneous size/original size) versus dimensionless time (time/burn-out time) to show the progress of oxidation mechanisms of lignite's. The aim is also verify the linear relationship and therefore justify or reject the assumption that chemical reaction is the controlling step or not.

2. Theory

A reaction is heterogeneous if it requires the presence of at least two phases to proceed at the rate that it does. It is immaterial whether the reaction takes place in one, two or more phases, at an interface, whether the reactants and products are distributed among the phases or are all contained within a single phase. Burning of lignite is a typical heterogeneous reaction as shown below [6].

$$\text{Lignite(s)} + \text{air(oxygen)} \rightarrow \text{fluid} + \text{solid products} \tag{1}$$

A common feature of all solid gas reaction systems is that the overall process may involve several intermediate steps as below.

Gaseous diffusion (mass transfer) of reactants and products from the bulk of the gas phase to the internal surface of the reacting solid particle;
Diffusion of gaseous reactants or products through the pores of a solid product or through the pores of partially reacted solid;
Adsorption of the gaseous reactants on and desorption of reaction products from the solid surfaces;
The actual chemical reaction between the absorbed gas and solid.

In studying gas–solid reactions it is concerned with four phenomena; external mass transfer, pore diffusion, adsorption/desorption and chemical reaction. Chemical kinetics basically deals with the rate of attainment of the end products, while reaction mechanism controls the overall rate of reaction. Since more than one phase is present in heterogeneous reactions, the movement of material from phase to phase must be considered in the rate equation. Thus, the rate expression in general will incorporate the mass transfer in addition to the usual chemical kinetics terms of homogeneous reactions. These mass transfer terms are different in the type and numbers in the different kinds of heterogeneous systems. For the non-catalytic reactions of slid particles with the surrounding fluid two models have been suggested in literature [7].

The continuous reaction model
The unreacted core model

Evidence from a wide variety of situations indicates that the unreacted core model approximates coal burning closely. Here the reaction occurs first at the outer skin of the solid particle. The zone of reaction then moves into the particle, leaving behind completely converted material and inert, which is referred to as ash. Thus, at any time during reaction, there exists an unreacted core of material, which shrinks in size during reaction. In the unreacted core model for combustion of lignite, four steps may occur in succession during the reaction. Since, these steps must occur successively for reaction to take place; we consider them to offer resistance in series. Because of this, if one of these steps offers the major resistance, that step may consider alone as the rate-controlling step. Therefore, basically three forms of rate expression can be developed pending on whether controlling step is:

Mass transfer of reactant through the boundary film,
Diffusion through ash,
Chemical reaction,

3. Experimental

In this research, TG/DTG experiments were conducted with Polymer Lab. 1500 thermal analysis unit. The TG/DTG experimental procedure involves placing 10 mg of sample, setting the heating and gas flow rate, and then commencing the experiments. All experiments were performed at a linear heating rate of 10°C/min over the temperature range of ambient to 900°C with an air flow rate of 50 ml/min. Prior to experiments TG/DTG was calibrated for temperature readings using calcium oxalate mono-hydrate as a reference material. It was also essential to calibrate the balance for buoyancy effects to allow quantitative estimation of weight changes. All the experiments were performed twice for repeatability. The samples used in this research were *Çayirhan, Tunçbilek* and *Soma* lignites prepared according to ASTM standards. Lignite samples were crushed to –10 mesh size, then different size fractions of the samples were obtained. Properties of the samples are given in Table 1.

4. Results and discussion

The kinetics and rate controlling steps of fluid–solid reaction, in this case lignite and air, can be found by following the progressive conversion of the solid particles and noting how particle size and operating temperature influence this conversion [7]. In this research it is postulated that chemical reaction is the controlling step for combustion of lignite. Thus, based on the unit surface of unreacted core, the rate equation for the stochiometry of Eq. (1) is;

$$-\left\{\left[\left(\frac{1}{4\pi r_c^2}\right)4\rho r_c^2\right]\left(\frac{d_{rc}}{d_t}\right)\right\} = -\rho\left(\frac{d_{rc}}{d_t}\right) = K_s C_{O_2} \tag{2}$$

on integration the above equation becomes,

$$t = \left(\frac{\rho}{K_s C_{O_2}}\right)(R - r_c) \tag{3}$$

the time τ required for complete reaction is given when $r_c = 0$ or,

$$\tau = \frac{(\rho R)}{K_s C_{O_2}} \tag{4}$$

combining Eqs. (3) and (4) yields,

$$\left(\frac{t}{\tau}\right) = 1 - \left(\frac{r_c}{R}\right) \tag{5}$$

Also,

$$W_c = \tfrac{4}{3}\pi r_c^3 \rho \tag{6}$$

$$W = \tfrac{4}{3}\pi R^3 \rho \tag{7}$$

Therefore,

$$\frac{r_c}{R} = \left(\frac{W_c}{W}\right)^{1/3} \tag{8}$$

and,

$$\left(\frac{t}{\tau}\right) = 1 - \left(\frac{W_c}{W}\right)^{1/3} \tag{9}$$

where; r_c = radius of unreacted core (cm), ρ = molar density of coal (0.0367 mol/cc), t = time (min), R = average radius of coal particle (125×10^{-4}), K_s = reaction rate constant based on unit surface area (cm/min), C_{O_2} = concentration of oxygen in the air (mol/cc), W_c = moles of unreacted core and W = original moles of core.

Table 1
Properties of lignite samples [8]

Sample	Moisture (%)	(VM + FC)[a] (%)	Ash (%)
Soma −30+18	5.72	50.82	43.46
Soma −18+10	6.40	51.99	41.61
Soma –10+0.5	6.64	52.78	40.58
Soma –0.5	6.99	51.58	41.43
Tunçbilek –30+18	2.48	44.73	52.79
Tunçbilek –18+10	2.30	43.80	53.90
Tunçbilek –10+0.5	2.69	47.26	50.05
Tunçbilek –0.5	2.40	41.28	56.32
Çayirhan –30+18	5.32	70.66	24.02
Çayirhan –18+10	5.00	66.16	28.84
Çayirhan –10+0.5	5.16	77.24	17.60
Çayirhan –0.5	6.34	72.73	23.90

[a] VF = volatile matter; FC = fixed carbon.

TG/DTG curves of *Çayirhan* lignite (−30+18 mesh size) is given in Fig. 1. The main characterzation point in the TG/DTG curve is the peak temperature where the rate of weight loss is at maximum. Beyond this peak (third peak, 735°C) the derivative curve falls rapidly and smoothly which is called burn-out temperature (780°C) which represents the temperature where sample oxidation is complete.

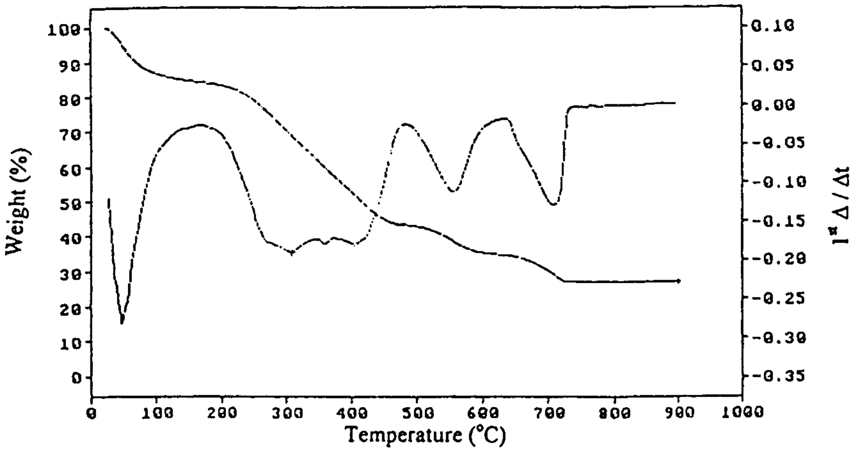

Fig. 1. TG/DTG curve of Çayirhan lignite sample (−30+18).

Table 2 represents the data which is converted into dimensionless time (instantaneous size/original size) versus dimensionless time (time/burn-out time) to show the progress of oxidation mechanisms of lignite's. r_c/R shows the instantaneous remaining wt.% of lignite whereas t/τ data is obtained from Eq. (9) (Fig. 2).

Table 2
(t/τ) versus (r_c/R) Values of Çayirhan lignite sample

t/τ	$(r_c/R)^a$	t/τ	$(r_c/R)^a$	t/τ	$(r_c/R)^b$	t/τ	$(r_c/R)^b$	t/τ	$(r_c/R)^c$	t/τ	$(r_c/R)^c$	t/τ	$(r_c/R)^d$	t/τ	$(r_c/R)^d$
0.228	0.921	0.499	0.770	0.228	0.930	0.499	0.779	0.228	0.935	0.499	0.782	0.228	0.945	0.499	0.785
0.240	0.918	0.511	0.766	0.240	0.927	0.511	0.775	0.240	0.932	0.511	0.778	0.240	0.942	0.511	0.781
0.251	0.912	0.522	0.764	0.251	0.923	0.522	0.773	0.251	0.928	0.522	0.776	0.251	0.938	0.522	0.779
0.262	0.909	0.533	0.762	0.262	0.920	0.533	0.771	0.262	0.925	0.533	0.774	0.262	0.934	0.533	0.777
0.273	0.904	0.545	0.761	0.273	0.915	0.545	0.770	0.273	0.920	0.545	0.773	0.273	0.928	0.545	0.776
0.285	0.899	0.556	0.758	0.285	0.910	0.556	0.767	0.285	0.915	0.556	0.770	0.285	0.922	0.556	0.773
0.296	0.893	0.567	0.756	0.296	0.904	0.567	0.765	0.296	0.909	0.567	0.768	0.296	0.915	0.567	0.771
0.307	0.887	0.578	0.752	0.307	0.898	0.578	0.761	0.307	0.902	0.578	0.764	0.307	0.908	0.578	0.767
0.319	0.881	0.590	0.747	0.319	0.892	0.590	0.756	0.319	0.896	0.590	0.759	0.319	0.901	0.590	0.762
0.330	0.877	0.601	0.741	0.330	0.888	0.601	0.750	0.330	0.890	0.601	0.753	0.330	0.894	0.601	0.756
0.341	0.869	0.612	0.735	0.341	0.880	0.612	0.744	0.341	0.882	0.612	0.747	0.341	0.886	0.612	0.750
0.353	0.863	0.624	0.730	0.353	0.874	0.624	0.739	0.353	0.876	0.624	0.742	0.353	0.879	0.624	0.744
0.364	0.857	0.635	0.724	0.364	0.868	0.635	0.733	0.364	0.870	0.635	0.736	0.364	0.872	0.635	0.740
0.375	0.850	0.646	0.721	0.375	0.861	0.646	0.730	0.375	0.863	0.646	0.733	0.375	0.865	0.646	0.736
0.386	0.844	0.606	0.718	0.386	0.855	0.606	0.727	0.386	0.857	0.606	0.730	0.386	0.858	0.606	0.734
0.398	0.837	0.669	0.716	0.398	0.848	0.669	0.725	0.398	0.850	0.669	0.728	0.398	0.851	0.669	0.732
0.409	0.830	0.680	0.715	0.409	0.841	0.680	0.724	0.409	0.843	0.680	0.727	0.409	0.844	0.680	0.731
0.420	0.821	0.692	0.714	0.420	0.832	0.692	0.723	0.420	0.835	0.692	0.726	0.420	0.836	0.692	0.730
0.432	0.813	0.703	0.713	0.432	0.824	0.703	0.722	0.432	0.827	0.703	0.725	0.432	0.828	0.703	0.729
0.443	0.809	0.714	0.712	0.443	0.816	0.714	0.720	0.443	0.819	0.714	0.723	0.443	0.820	0.714	0.727
0.454	0.797	0.725	0.710	0.454	0.807	0.725	0.718	0.454	0.810	0.725	0.721	0.454	0.812	0.725	0.725
0.466	0.789	0.737	0.707	0.466	0.798	0.737	0.715	0.466	0.801	0.737	0.718	0.466	0.804	0.737	0.722
0.477	0.781	0.748	0.704	0.477	0.790	0.748	0.712	0.477	0.794	0.748	0.715	0.477	0.796	0.748	0.718
0.488	0.775	0.759	0.700	0.488	0.784	0.759	0.707	0.488	0.788	0.759	0.710	0.488	0.790	0.759	0.712

[a] −30+18.
[b] −18+10.
[c] −10+00.5.
[d] −00.5.

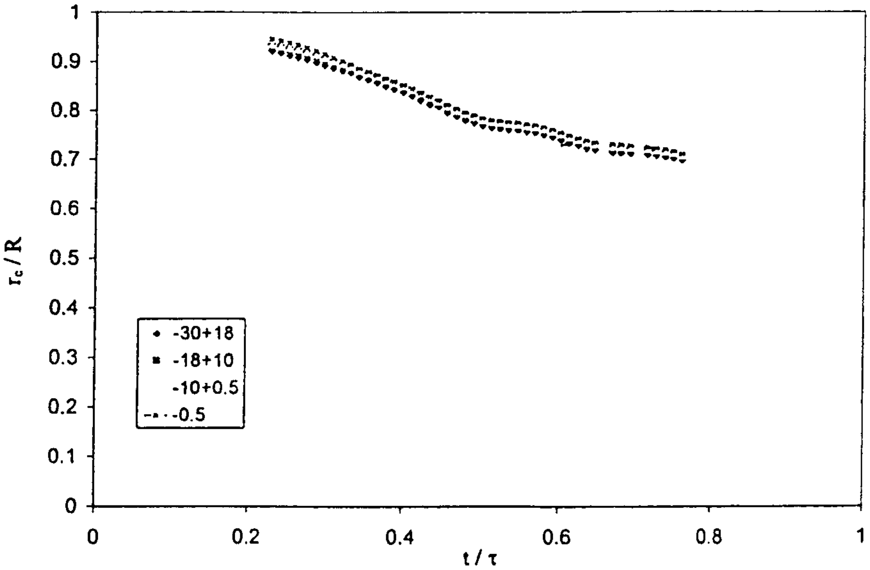

Fig. 2. r_c/R vs. t/τ curves of Çayirhan lignite sample at different sizes.

Lignites of different size studied in this research show mainly linear behaviour at elevated temperatures, which justifies the assumption that chemical reaction is the controlling step. This suggests that the kinetic parameters involved might be calculated on the basis of a single rate constant. It was also observed that as the particle size increased (from –0.5 to –30+18) the linearity behaviour of the samples is decreased. Therefore, a composite rate might be needed to model the progress of oxidation.

5. Conclusions

On the basis of comparing the oxidation mechanisms of lignite samples of different size using the data obtained from TG/DTG experiments, it could be said that linear behaviour at elevated temperatures justifies the assumption that chemical reaction is the controlling step.

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