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EFFECT OF DIFFERENT BINDERS ON THE COMBUSTION PROPERTIES OF LIGNITE
Part II. Effect on kinetics

N. E. Altun[1], *M. V. Kök*[2] *and C. Hicyilmaz*[1]

[1]Department of Mining Engineering, Middle East Technical University, 06531, Ankara, Turkey
[2]Department of Petroleum and Natural Gas Engineering, Middle East Technical University, 06531, Ankara, Turkey

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Abstract

In this research kinetic analysis of the Tuncbilek lignite and its mixture with different binders (molasses, CMC, sulphide liquor, heavy crude oil, sodium silicate, cornstarch, lime, peridur, bentonite, cement and poly(vinyl-acetate)) were analysed by thermogravimetric (TG/DTG) methods. Two different kinetic models (Arrhenius and Coats–Redfern) were used to determine the activation energies of the samples studied. The concept of weighed mean activation energy was applied to determine the overall reactivity of the samples. It was observed that molasses, CMC, heavy crude oil, peridur, bentonite and poly(acetate) decreased the activation energy of the coal sample, whereas, all other binders increased the activation energy of the coal sample.

Keywords: binder, coal, combustion, kinetics, thermogravimetry

Introduction

It is well recognised that thermogravimetry (TG/DTG) and differential scanning calorimetry (DSC) are rapid tools which have been used in a wide variety of areas related to proximate analysis, coal reactivity, heat effect associated with coal pyrolysis, combustion and kinetics. Thermal analysis enables physical and chemical phenomena occurring in the substance investigated during heating. The theoretical principles for calculating kinetic parameters are based mainly on investigations of the energy and mass changes at a constant temperature or at a variable temperature.

Gold [1] has 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 the magnitude of the exothermic peak were strongly affected by the heating rate, sample mass and the particle size. Morgan and Robertson [2] determined coal-burning profiles by thermogravimetric analysis. They have claimed that kinetic parameters from Arrhenius plots of the profiles cannot be readily related to any specific stage of combustion. However, some features of the

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profiles are clearly related to coal properties, and correlation exists between unburnt carbon loss as predicted from high temperature oxidation rates and characteristic temperature of the thermogravimetric profile. Crelling *et al.* [3] determined the combustion properties of separated single coal maceral fraction from a rank series of coals and then tried to predict the combustion behaviour of various whole coals on the basis of their maceral composition and rank. Rai and Tran [4] conducted a kinetic study on non-catalysed and catalysed coal. In their kinetic model, the apparent activation energy is measured to be a rectilinear function of the extent of reaction. The order of reaction was found to be about 0.3 for the pyrolysis step and 0.67 for the hydrogasification step. Cumming [5] has developed a method for describing the reactivity or combustibility of solid fuels, such as lignite, bituminous coal and petroleum coke, in terms of weighed mean apparent activation energy, derived from simultaneous TG/DTG readings. He proposed that the mean activation energy method be the establishing method that involves recording overall temperatures on the burning profile curve. Smith and Neaval [6] carried out coal combustion experiments in the temperature range 25–900°C using air atmospheric pressure in a derivative thermogravimetric analysis system. Sixty-six coals high in vitrinite and low in inorganic were examined as part of a coal characterisation program. The rate data were fitted to an Arrhenius equation and plots showed four distinct regions of combustion. Calculated apparent activation energies were of the correct orders of magnitude to describe combustion regions corresponding to chemical-reaction-controlled as well as diffusion-controlled processes. Patel *et al.* [7] measured the rate of combustion of lignite char using TG over a range of oxygen concentration (5–20%) and at temperatures between 325–650°C. The activation energy in the chemical rate-controlled zone was 120 kJ mol^{-1} and the transition to film diffusion control occurred at 430°C. The Arrhenius plots indicated no region of pore diffusion control. Serageldin and Pan [8] developed a linear relationship between activation energy and heat of reaction. The effects of alkali metal salts on the decomposition of coal fewer than three different atmospheres (nitrogen, CO_2 and air) are also investigated. The effect of the catalysts on coal conversion and CH_4, CO_2 and CO emissions are related to observed changes in the activation energy.

Experimental

In this research, TG/DTG experiments were conducted with a Polymer Lab. 1500 thermal analysis unit. The TG/DTG experimental procedure involves placing the sample (~25 mg), setting the heating rate (10°C min^{-1}) and air flow rate (15 mL min^{-1}), then commencing the experiments. All the experiments were performed in a temperature range of 25–900°C. Prior to experiments the equipment was calibrated for temperature readings. The balance was also calibrated for buoyancy effect, allowing qualitative estimation of mass changes. Calorific values of the samples were measured by a bomb calorimeter according to the ASTM standards.

In this research Tuncbilek lignite sample was used. R.O.M lignite sample was crushed to a particle size of –212 micron to get mixed homogeneously with different binders. Molasses, sulphide liquor, CMC, crude oil, cornstarch (caustisized with NaOH), lime, bentonite, cement, peridur and their mixtures in different ratios were used.

Kinetic analysis

In this study, thermogravimetric data were analysed according to an Arrhenius and Coats–Redfern models. Application of Arrhenius model [9, 10] to the TG/DTG curves is easy and fast. So the equation of Arrhenius-type kinetic model takes the following form.

$$-\mathrm{d}W/\mathrm{d}t = kW^{\mathrm{n}} \tag{1}$$

$$k = A_{\mathrm{r}}\exp(-E/RT) \tag{2}$$

Assuming first-order kinetics,

$$-\mathrm{d}W/\mathrm{d}t = A_{\mathrm{r}}\exp(-E/RT)W \tag{3}$$

$$[-(\mathrm{d}W/\mathrm{d}t)1/W] = A_{\mathrm{r}}\exp(-E/RT) \tag{4}$$

Taking the logarithm of both sides,

$$\log[-(\mathrm{d}W/\mathrm{d}t)1/W] = \log A_{\mathrm{r}} - E/2.303\,RT \tag{5}$$

where $\mathrm{d}W/\mathrm{d}t$ is the rate of mass change, E is the activation energy, T is the temperature, A_{r} is Arrhenius constant and n is the reaction order.

When $\log[(\mathrm{d}W/\mathrm{d}t)1/W]$ is plotted *vs.* $1/T$, a straight line is obtained which will have a slope equal to $E/2.303R$ and from the intercept the Arrhenius constant can be estimated.

Coats and Redfern [11] developed an integral method, which can be applied to TG/DTG 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 analysis;

$$\ln[1-(1-\alpha)^{1-\mathrm{n}}/(T^2(1-n))] = \ln[(AR/(\beta E)(1-2RT/E)] - [E/(RT)] \tag{6}$$

where β is the heating rate.

Thus a plot of $\ln[1-(1-\alpha)^{1-\mathrm{n}}/(T^2(1-n))]$ *vs.* $1/T$ should result in a straight line of slope equals $-E/R$ for the correct value of reaction order (n).

The individual activation energies for each reaction region can be notionally attributed to different reaction mechanisms, but they do not give any indication of the contribution of each region to the overall reactivity of the coal. Therefore, the concept of weighed mean activation energy, E_{wm}, as applied to determine the overall reactivity of the coal [5].

$$E_{\mathrm{wm}} = F_1E_1 + F_2E_2 + F_3E_3 + \ldots + F_{\mathrm{n}}E_{\mathrm{n}} \tag{7}$$

where F_1, F_2, … are the mass fractions of the combustible content of the sample burned during each region of Arrhenius linearity, and E_1, E_2, … are the individual apparent activation energies obtained over each region.

Results and discussion

Modelling of reaction kinetics for a combustion process is extremely complicated, because several components are simultaneously oxidised. In this study, two different

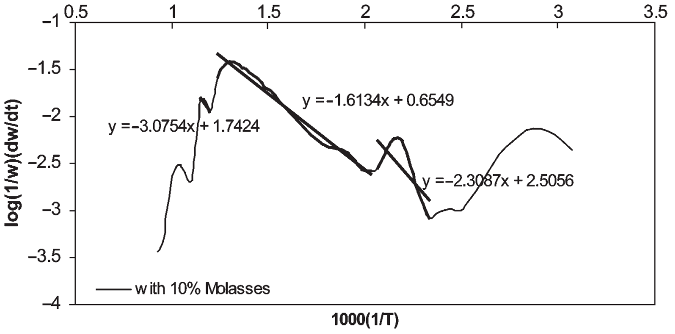

Fig. 1a log(1/*w*)(d*w*/d*t*) *vs.* 1/*T* curve of 10% molasses added sample

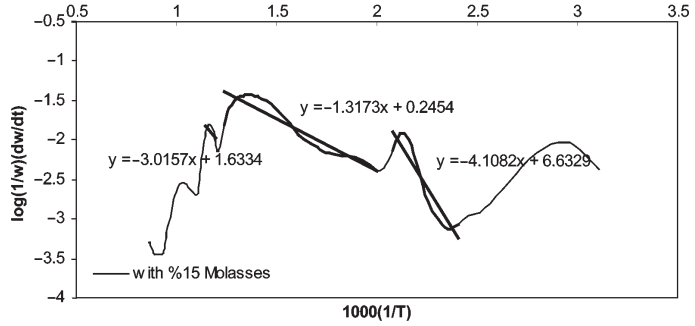

Fig. 1b log(1/*w*)(d*w*/d*t*) *vs.* 1/*T* curve of 15% molasses added sample

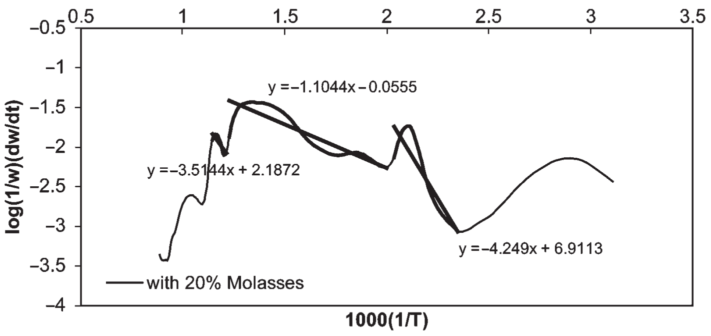

Fig. 1c log(1/*w*)(d*w*/d*t*) *vs.* 1/*T* curve of 20% molasses added sample

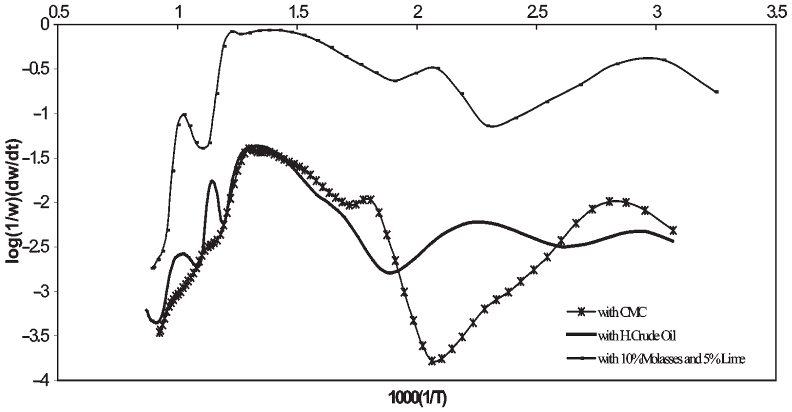

Fig. 2 log(1/*w*)(d*w*/d*t*) *vs.* 1/*T* for CMC, heavy crude oil and 5% lime+10% molasses added samples

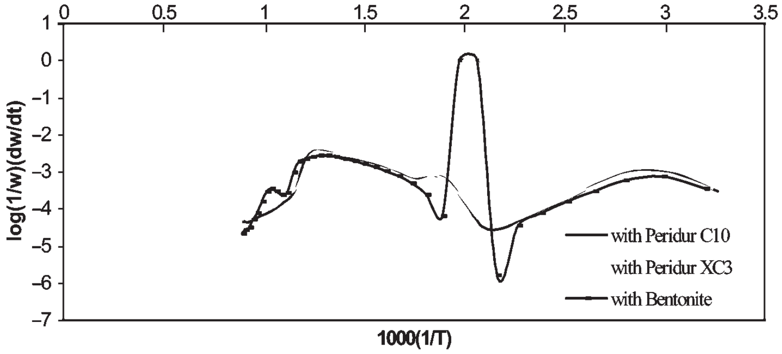

Fig. 3 log(1/*w*)(d*w*/d*t*) *vs.* 1/*T* curves for peridur C10, peridur XC3 and bentonite added samples

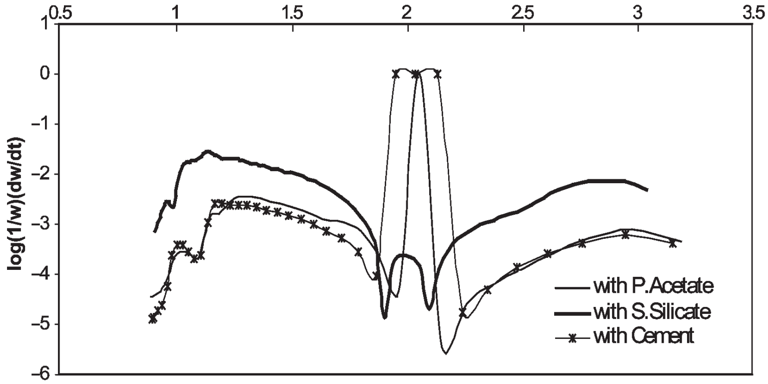

Fig. 4 log(1/*w*)(d*w*/d*t*) *vs.* 1/*T* curves for P. acetate, S. silicate and cement added samples

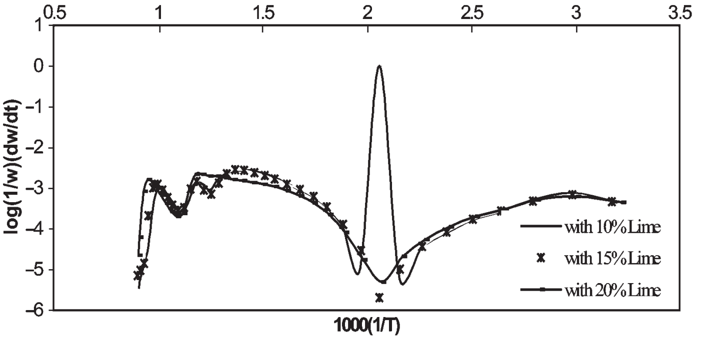

Fig. 5 log(1/*w*)(d*w*/d*t*) *vs.* 1/*T* curves for lime added samples

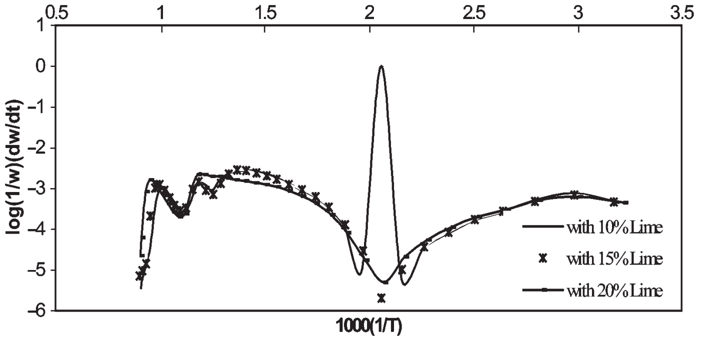

Fig. 5 log(1/*w*)(d*w*/d*t*) *vs.* 1/*T* curves for lime added samples

kinetic models (Arrhenius and Coats–Redfern) were used to determine the activation energies of the samples studied. The weighed mean activation energy concept was applied to determine the overall reactivity of the samples. In Arrhenius model, it is assumed that the rate of mass loss of the total sample is dependent only on the rate constant, the sample mass remains and the temperature with reaction order of unity. The mean activation energy of Tuncbilek lignite sample was found as 17.6 kJ mol^{-1}. A general decrease is observed in the activation energy of the Tuncbilek lignite (Fig. 1) with an increase in the mass percent (10, 15 and 20%) of molasses (15.1, 13.4 and 11.5 kJ mol^{-1}, respectively). 10% reduction in the activation energy of the Tuncbilek lignite sample was observed with the addition of both CMC and heavy crude oil (Fig. 2). An additional peak around 200°C (initiation of the combustion of lignite) in the mixture of coal with molasses, CMC and heavy crude oil was observed, which may be the main reason for the reduction in activation energy value of the Tuncbilek lignite sample. A reduction in the activation energy of Tuncbilek lignite was also observed with other binders as peridur and bentonite (Figs 3 and 4). On the other hand, sodium silicate, lime and cement caused an increase in the activation energy of the Tuncbilek lignite (Fig. 4). A general increase is observed in the activation energy of the Tuncbilek lignite (Fig. 5) with an increase in the mass percent (10, 15 and 20%) of lime (21.8, 22.8 and 23.1 kJ mol^{-1}, respectively).

Table 1 Activation energies according to the Arrhenius and Coats–Redfern models

Type of binder	Activation energy, Arrhenius model/kJ mol^{-1}	Activation energy, Coats– Redfern model/kJ mol^{-1}
Tuncbilek coal	17.6	19.8
Molasses 10%	15.0	18.1
Molasses 15%	13.3	16.7
Molasses 20%	11.5	14.9
CMC	16.1	17.8
S. liquor	20.3	22.6
Heavy oil	16.0	19.1
S. silicate	18.1	20.4
Cornstarch	20.2	26.4
Lime 10%	21.8	23.6
Lime 15%	22.8	24.2
Lime 20%	23.1	25.9
Peridur C10	16.1	17.1
Peridur XC3	15.8	16.3
Bentonite	14.4	13.6
Cement	17.6	18.9
Lime 5%+Molasses 10%	9.3	12.1
P. acetate	14.5	14.8

Coats–Redfern developed an integral method, which can be applied to TG/DTG 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. In this research four different reaction orders (1/2, 2/3, 1 and 3/2) were assumed and in all the experiments best linear plot was observed in unity reaction order. Same trends were observed in the activation energy values of all the samples studied. Table 1 represents the activation energy values of the samples for both of the models studied.

References

1 P. I. Gold, Thermochim. Acta, 42 (1980) 244.
2 P. A. Morgan and S. D. Robertson, Fuel, 65 (1986) 1546.
3 J. C. Crelling, E. J. Hippo, A. Woerner and D. P. West, Fuel, 71 (1992) 151.
4 C. Rai and D. Q. Tran, Fuel, 58 (1977) 603.
5 J. W. Cumming, Fuel, 63 (1980) 1436.
6 E. S. Smith and C. R. Neaval, Fuel, 60 (1981) 458.

7 M. M. Patel, D. T. Grow and B. C. Young, Fuel, 67 (1988) 165.
8 M. A. Seragaldin and W. Pan, Thermochim. Acta, 76 (1984) 145.
9 M. V. Kök, Thermochim. Acta, 214 (1993) 315.
10 M. V. Kök, E. Ozbas, C. Hicyilmaz and S. Bilgen, Thermochim. Acta, 302 (1997) 125.
11 W. Coats and P. Redfern, Nature, 201 (1964) 68.