Coal pyrolysis: thermogravimetric study and kinetic modelling

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Abstract

In this experimental study on coal pyrolysis it was found that heat transfer and heating rate have an important influence on the results obtained. A model has been developed which takes into account these aspects. The kinetic parameters were determined using a differential method and the experimental data obtained at low heating rates. The agreement between the predictions of the model, for any heating rate, and the experimental values is fairly good.

LIST OF SYMBOLS

A	frequency factor (s^{-1})
c_p	specific heat of the coal crucible $(J\ kg^{-1}\ K^{-1})$
E	activation energy $(J\ mol^{-1})$
k	kinetic coefficient (s^{-1})
M_f	mass of volatile compounds lost during the complete reaction (dry basis) (mg)
M_p	mass of volatile compounds lost (dry basis) (mg)
m	mass of coal plus crucible (kg)
R	gas constant $(J\ mol^{-1}\ K^{-1})$
S	crucible surface area (m^2)
T	reaction temperature (K)
T_{max}	temperature at the maximum of the DTG plot (K)
T_w	temperature of furnace wall (K)
t	time (s)
X	fractional conversion (dry basis)
β	parameter of eqn. (7) $(s^{-1}\ K^{-3})$
ε	emissivity
ϕ	heating rate $(K\ min^{-1}\ or\ K\ s^{-1})$
σ	Stefan–Boltzmann constant $(W\ m^{-2}\ K^{-4})$

INTRODUCTION

Coal pyrolysis is an important process, not only as a treatment for sulphur elimination from coal, but also because it is the first step in combustion and gasification processes, to which much research effort is devoted.

A knowledge of pyrolysis kinetics is, therefore, very interesting. A number of communications have dealt with this subject; most of them have proposed mathematical models based in isothermal operating conditions, with very different reacting mechanisms of diverse complexity. However, dynamic models are more appropriate for this process because they take into account the heating rate; this rate is often considered to be constant, i.e. the operating temperature is supposed to increase at a given velocity. If pyrolysis is done at a non-constant heating rate, the mathematical modelling becomes more complex and difficult to solve. In such cases a single thermal decomposition reaction is usually considered.

In the present work we developed a dynamical pyrolysis model which takes into account three different groups of thermal decomposition reactions. While the inclusion of the three groups makes the model closer to the real process, it implies an additional difficulty, as the mass of reactants undergoing each reaction must be known. A simple procedure is proposed for determining the kinetic parameters. The model was tested using experimental data and the agreement found was fairly good.

EXPERIMENTAL SET-UP

The coal pyrolysis was done using a thermogravimetric analyser (Setaram, TG-85) with which the mass loss (thermogravimetric (TG) signal) and the rate of mass loss (differential thermogravimetric (DTG) signal) as a function of time or temperature were recorded. A schematic diagram of the apparatus is given in Fig. 1. The main features of the analyser are summarized in Table 1.

The coal used in the study was a lignite from Figols (Catalonia, Spain) with a particle size of 750–1200 μm; the sample mass (free of moisture) used was 145 mg, and the sample was located in a ceramic crucible. The operating temperatures ranged from 973 K to 1223 K; nitrogen at atmospheric pressure was used (5 1 h^{-1}). Two different operating procedures were used. (1) The sample was placed inside the furnace and heated at constant heating rate to the operating temperature (the sample and the furnace were heated together); the heating velocity ranged from 3 to 90 K min^{-1}. (2) The furnace was heated to the operating temperature and the sample then introduced. The sample thus underwent sudden heating, its temperature varying non-linearly with time. Of course, the variation in
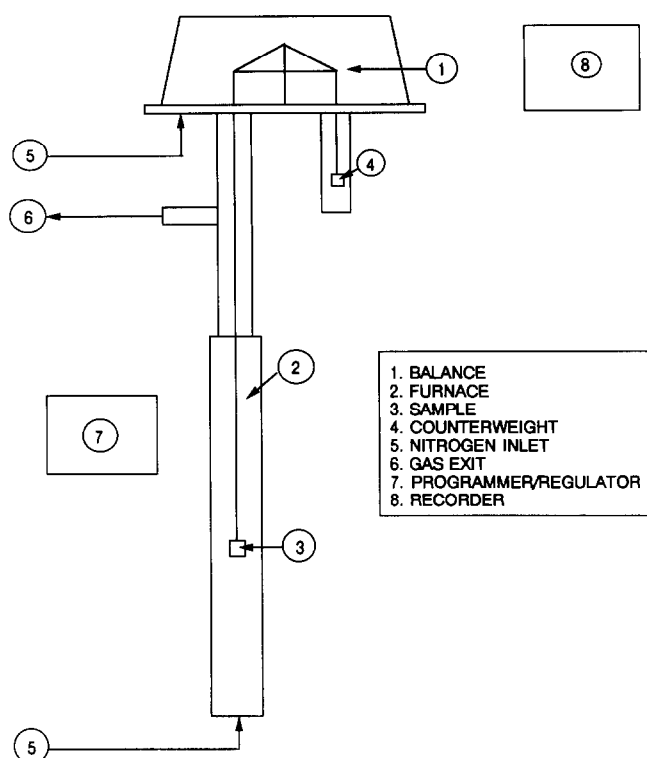
Fig. 1. Schematic diagram of the experimental set-up used in the study.

temperature with time depends on the experimental set-up and on the operating mode used.

EXPERIMENTAL RESULTS

If the heating rate used is constant, then the sample temperature at any moment is known, as it is practically the same as the furnace temperature. The rate of mass loss as a function of temperature for different heating rates, with a final operating temperature of 1223 K, is shown in Fig. 2. At low heating rates three peaks were observed, which correspond to the three groups of thermal decomposition reactions which take place at these

TABLE 1

Features of the thermogravimetric analyser used in the study

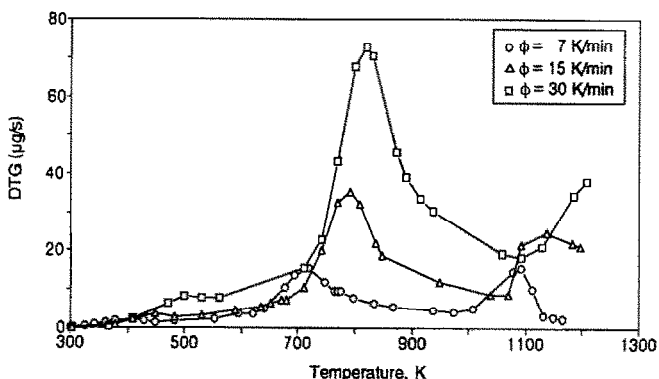|	
Operating temperature	20–1000 K
Heating rate	0–99.99 K min^{-1}
Balance sensitivity	$\pm 10\ \mu$g
Shunt sensitivity	$\pm 5\ \mu$g
Ceramic crucible dimensions	length 1 cm, internal diameter 0.6 cm

Fig. 2. The DTG curves obtained at different heating rates.

temperatures. The first group corresponds to the loss of light molecules which are linked physically to the coal. At higher temperatures the breaking of thermal decomposition bonds occurs, originating the formation of tar and hydrocarbons of high molecular weight. Finally, at higher temperatures the coking of coal occurs. These results are in good agreement with those obtained by Ibarra et al. [1].

As the heating rate was increased, the peaks became less well defined; at higher heating rates the peaks completely overlapped and only a single peak was observed (Fig. 2), as if only a single reaction had taken place. Thus it is evident that the kinetic parameters corresponding to the different reactions can be determined only at low heating rates. Under such conditions the thermal inertia is negligible and the sample temperature is really that established by the heating programme [2–5], as the time allowed was sufficient for the sample temperature to reach the furnace temperature. At higher heating rates, the sample temperature follows the furnace temperature but in a less uniform way; less time is required to reach the different peaks and, therefore, the peaks overlap. A kinetic study done at high heating rates would thus lead to incorrect results; this is why in studies where equipment operating at high heating rates has been used the results have been interpreted as coal pyrolysis comprising only a single reaction.

In the present work the activation energy (E) and the frequency factor (A) were determined for each reaction from the data obtained at low heating rates. The mass lost in each thermal decomposition reaction was determined using A and E; this information was then applied to dynamic operating conditions, with variable heating rates.

DYNAMIC KINETIC MODEL

The kinetic parameters of the thermal decomposition reaction were calculated using a differential method [6], taking into account the heating

rate and assuming that: (1) three parallel reactions exist [7]; (2) the kinetic equations of each reaction are of first order [8]; (3) the rate constants follow the Arrhenius law; and (4) at low heating rates the sample temperature can be considered to be equal to the furnace temperature.

The following expressions can therefore be established.

$$\frac{dX_i}{dt} = k_i(1 - X_i) \tag{1}$$

where i indicates reaction 1, 2 or 3, with $X_i = M_{pi}/M_{fi}$.

$$\frac{dX_i}{dt} = A_i \exp(-E_i/RT)(1 - X_i) \tag{2}$$

Introducing $\phi = dT/dt$

$$\frac{dX_i}{dT} = \frac{A_i}{\phi} \exp(-E_i/RT)(1 - X_i) \tag{3}$$

and setting the second derivative equal to zero

$$\ln\left(\frac{\phi}{T_{max}^2}\right) = \ln\left(\frac{A_i R}{E_i}\right) - \frac{E_i}{RT_{max}} \tag{4}$$

A plot of $\ln(\phi/T_{max}^2)$ vs. $1/T_{max}$ (where T_{max} is the temperature at the maximum of the DTG plot for different heating rates) gives a straight line for each of the three observed reactions. The slope of such a plot allows the determination of the activation energy, and the intersect of the three lines gives the value of the frequency factor. In this way the kinetic parameters can be determined for each thermal decomposition reaction (Fig. 3) and the overall mass which can be lost during each reaction if they are completed can be determined by integrating each peak in the DTG plot
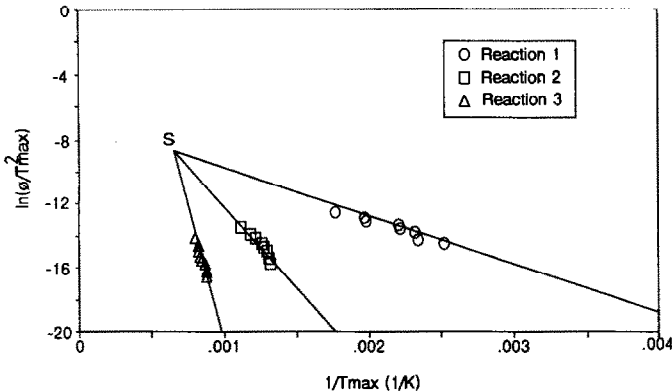

Fig. 3. Determination of the kinetic parameters.

TABLE 2

The kinetic parameters and the mass of volatile compounds lost during the whole reaction

Reaction	A (s^{-1})	E (J mol^{-1})	M_f (mg)
1	2.9	24750	3.6
2	1230	82485	26
3	7.56E10	291270	14.2

obtained at a low heating rate (for example, $\phi = 3$ K min^{-1}). The results obtained in this way are listed in Table 2.

The effect of heating rate on the peak overlap can be seen from Fig. 3. As the heating rate increases, the three reactions converge to the same point, as can be seen in the DTG plot (Fig. 2). This convergence point (point S in Fig. 3) indicates the lowest value of the heating rate at which a single peak (and, therefore, a single "reaction") will be obtained. For the lignite used in this work, this value was $\phi = 390$ K s^{-1}. This explains why different kinetic results are obtained for the pyrolysis with the use of different heating rates.

Model for constant heating rate

If the values of the activation energy, frequency factor and overall mass loss are known, the differential equation can be integrated for each thermal decomposition reaction:

$$\int_0^{X_i} \frac{\mathrm{d}X_i}{(1-X_i)} = A_i \int_0^t \exp(-E_i/RT)\,\mathrm{d}t \tag{5}$$

The integration of the second term in the kinetic equation can be solved numerically (as the variation of temperature as a function of time is known)
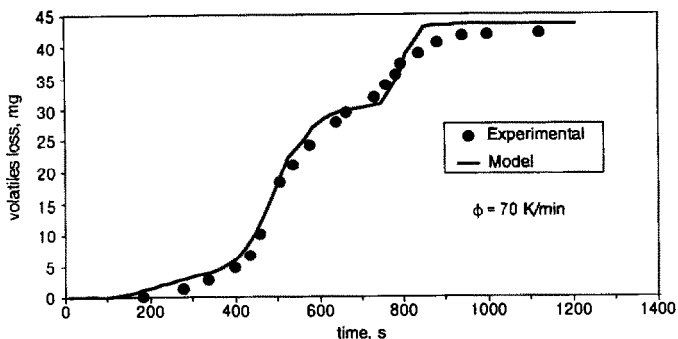

Fig. 4. Comparison between the experimental data and the values predicted using the model for a constant heating rate.

by series, or through empirical methods. In the present work this integration was done using the Simpson method, which is probably the most accurate. The values obtained using model and the experimental values obtained at a heating rate of 70 K min^{-1} are compared in Fig. 4. It can be seen that the predictions of the model obtained using the kinetic parameters measured at low heating rates are in good agreement with the experimental values.

Model for variable heating rate

As in this case the variation in temperature as a function of time must be determined, a thermal model is required which accounts for the influence of the main features of both the experimental set-up and the operating conditions.

Some authors [9,10] have assumed that the kinetic parameters change with the heating rate. Such a conclusion could be derived from Fig. 5, for example, where the experimental mass loss is plotted as a function of time; an influence of heating rate seems really to exist. However, this influence is in fact due to the thermal effect, which masks the true kinetic behaviour of the system.

In order to measure the variation in the temperature of the sample, a small thermocouple (type K) was introduced inside the crucible. This allowed us to obtain a plot of temperature vs. time (Fig. 6) for each final operating temperature (from 873 to 1223 K). Using the geometrical arrangement of the system and these results, the radiation was modelled in order to determine the relationship between temperature and time.

The crucible was considered to be a small grey body surrounded by a larger one (the furnace). This hypothesis leads to the expression

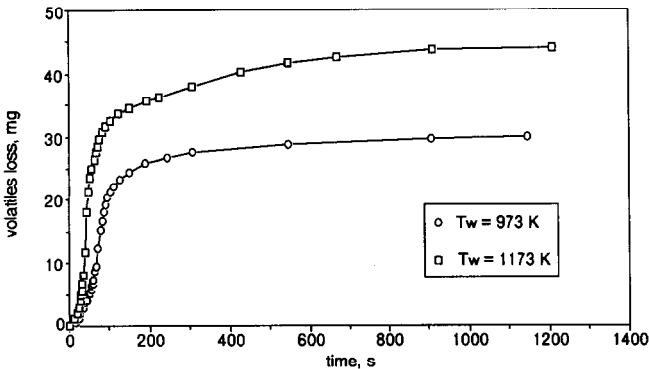$$mc_p \frac{dT}{dt} = \sigma S \varepsilon \left(T_w^4 - T^4 \right) \tag{6}$$

Fig. 5. The loss of volatile compounds at different temperatures of the furnace wall (variable heating rate).
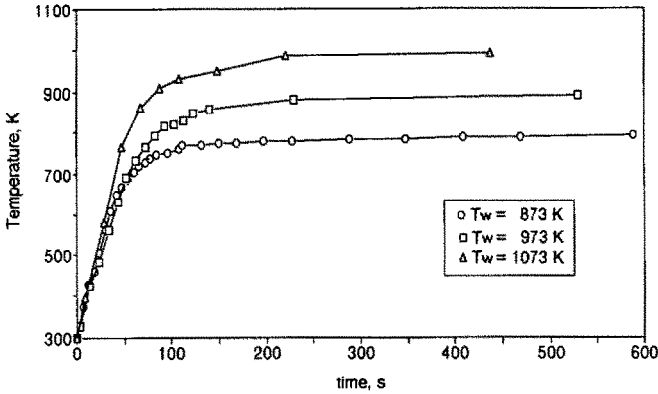
Fig. 6. Plot of sample temperature vs. time at different temperatures of the furnace wall.

which can be transformed to

$$\frac{dT}{(T_w^4 - T^4)} = \beta \, dt \tag{7}$$

The value of the parameter β can be established from the experimental data by plotting temperature vs. time. The agreement between values predicted using the model and the experimental data is shown in Fig. 7.

Once the thermal behaviour has been modeled, it is possible to develop the kinetic model; this should be similar to that proposed for the case of constant heating rate, although the sample heating is now due to radiation.

The kinetic equation can be written as

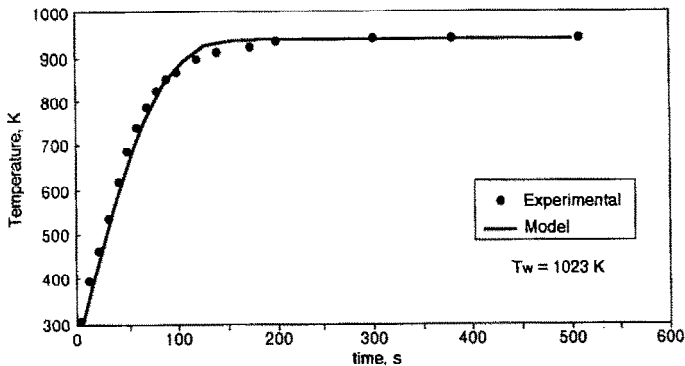$$\frac{dX_i}{dt} = A_i \exp(-E_i/RT)(1 - X_i) \tag{8}$$

Fig. 7. Sample temperature: comparison between experimental data and the values predicted using the thermal model.
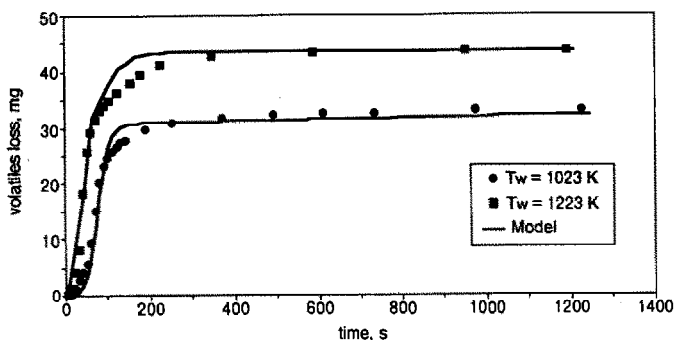
Fig. 8. Comparison between the experimental data and the values predicted using the model at different variable heating rates.

and, therefore,

$$\int_0^{X_i} \frac{dX_i}{(1-X_i)} = A_i \int_0^t \exp(-E_i/RT) \, dt \qquad (9)$$

The kinetic parameters are known as they are the same as those already determined at constant and low heating rates.

The temperature at any instant was measured by applying the Newton–Raphson method; these values were then introduced into the integral, which was solved using the Simpson method. The values predicted using this model are compared with the experimental data in Fig. 8. It can be seen from this figure that if the thermal effects are separated and taken into account by means of the appropriate model, the kinetic data obtained at constant heating rates can also be applied to those situations in which high heating rates are used.

CONCLUSIONS

The thermogravimetric analysis undertaken in this study shows that the pyrolysis of the lignite can be considered to comprise a set of three parallel thermal decomposition reactions, all of which have first-order kinetics. The only way to determine the kinetic parameters is to operate at low heating rates, which minimizes the thermal inertia of the system and assures a uniform heating rate of the particles.

Using a differential method and the experimental data obtained at low heating rates, the kinetic parameters and the total mass loss were determined for each thermal decomposition reaction. These values can be applied to other runs, operating at any constant or variable heating rate. Furthermore, this method allows the determination of the lowest value of the heating rate at which a single peak will be obtained, which corresponds

to what is usually called "rapid pyrolysis"; however, even in this case the kinetic parameters can be applied.

The results obtained using the proposed method show that the variety of pyrolysis models found in the literature is due not only to the different types of coal used, but also to the fact that many workers have neglected the influence of heat-transfer features or have operated at high heating rates. In the latter case the models involve an error which can be very important.

The procedure proposed in the present work models more closely the real pyrolysis process. Its use is not restricted to coal pyrolysis but can be applied to any gas–solid reaction.

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