Factors influencing the spontaneous heating of low-rank coals

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Abstract

Two quantities relevant to self heating—activation energy of ignition and thermal diffusivity—have been measured for three different Thai lignites and for a sample of an Australian lignite for comparison. Activation energies of the order of 10^2 kJ mol^{-1} are reported with some spread evident. Thermal diffusivities of the order of 2×10^{-7} m^2 s^{-1} are also reported and are compared with existing values for related materials.

1. Introduction

The tendency of coals when stockpiled or transported to self-heat is well known in the industry and in the early years of the present century guidelines were laid down [1] which aimed to minimise self-heating. It was recognised at that time that the factors central to coal stockpile thermal safety were (i) the intrinsic reactivity of the coal to oxygen, and (ii) heat transfer within the assembly of coal.

Investigations of coal self-heating in relatively recent years have been fairly plentiful, and techniques employed have included the crossover method [2], where relative propensities to self-heating are assessed on the basis of time taken for the various samples to attain a particular temperature under the influence of applied heat. Another common technique [3] uses Dewar flasks containing the coal under examination together with a stream of oxygen. Conditions for ignition or otherwise can be deduced, and, it is intended, at least relative reactivities of various samples can reliably be assessed.

Whilst each of these places emphasis on coal reactivity as the key factor, a recent contribution by De Faveri et al. [4] considers heat 'propagation' within assemblies of coal particles, and presents temperature–time trajectories for coal samples experiencing applied heat under both inert and oxidising condi-

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tions. Quite apart from its obscurities of detail, the work of De Faveri et al. is open to serious criticism on purely conceptual grounds in that results under inert and oxidising conditions are compared on the basis of their conformity to a model in which only heat transfer, and not heat generation, is considered. Moreover, as we shall show in this paper, a straightforward technique exists for *rigorous experimental measurement* of the quantity influencing heat propagation viz., coal thermal diffusivity, α, defined as $\alpha = k/c\sigma$ (see notation) where k is the thermal conductivity, c the heat capacity, and σ the bulk density.

This paper presents thermal diffusivity values for four coals: one from Victoria, Australia and three from Thailand. These particular coals were chosen because they are low-rank coals, and it is widely known that such coals have a greater propensity to self-heating than more mature coals, and hence make a suitable subject for investigations concerned with self-heating. In addition to the heat transfer measurements, activation energy values for the ignition of the respective coals are presented. These were measured by basket heating, identification of the conditions for ignition and application of ignition theory, as described in the experimental account below.

Hence the data presented herein provide insight into both reactivity and heat propagation for each of four samples of coal, and afford a basis for possible further investigations based on quantitative heat balance considerations.

Experimental

(i) Reactivity measurements

Activation energies of ignition were measured by basket heating of samples of the respective coals in an oven, determination of critical conditions for an ignition and application of the Frank–Kamenetskii model of thermal ignition. This procedure has been used by the present group [5] and other [6, 7] for materials as diverse as activated carbons and poultry feed. A summary of the method as it relates to the materials which are the subject of this paper is given below, and the reader is referred to other work [6, 8] for a fuller discussion.

The procedure is for steel gauze baskets of various sizes (e.g., 4, 6, 8 cm side cube) to be filled with the material under examination at a known density. By trial and error with a particular basket size in a recirculating air oven, $(T_0)_{\text{crit}}$, the critical ambient temperature at which ignition behaviour sets in, can be deduced. The procedure is repeated for other sizes of basket, and to the results is applied the following equation which follows from the Frank–Kamenetskii model:

$$\ln\left[\frac{\delta_{\text{crit}}(T_0)^2_{\text{crit}}}{\sigma r_0^2}\right] = \ln\frac{qE_aA}{Rk} - \frac{E_a}{R(T_0)_{\text{crit}}} \tag{1}$$

where δ_{crit} is the Frank–Kamenetskii parameter and r_0 the corresponding radius, q is the heat of reaction, E_a is the activation energy of ignition, A is the

pre-exponential factor and R is the gas constant. The value of the Frank–Kamenetskii parameter δ_{crit} and the corresponding radius r_0 are obtainable from the literature and for a cubic assembly of reactant, as used in the present work, have values as follows [6, 8]

$$\delta_{crit} = 3.663 \text{ and } r_0 = 1.194 \times \text{half-width}$$

If $\ln[\delta_{crit}(T_0)_{crit}^2/\sigma r_0^2]$ is plotted against $1/(T_0)_{crit}$, the result is a straight line of slope $-E_a/R$, from which a value for the activation energy can be deduced. A thermocouple (type K, chromel/alumel) in the centre of the reacting sample, connected to a hybrid (digital/analogue) recorder, enables the thermal behaviour of the sample to be continuously monitored, and so critical conditions are easily identified.

(ii) Thermal diffusivities

Measurement of thermal diffusivities made use of a technique described by Nordon and Bainbridge [9], who were concerned with thermal diffusivities of packed beds of char. The method has since been applied to other materials including forest floor litter [10]. The experimental procedure involves transferring a sample from a bath at a particular temperature to another bath at a different temperature. The thermal diffusivity is then obtainable from the heating or cooling curve by means of a treatment outlined in Appendix I and discussed more fully by Nordon and Bainbridge. Either heating or cooling curves can be used, and in fact both were used in the present examination of low-rank coals. The method is a single-point determination, and a test of its validity is outlined in the Appendix.

A cylindrical vessel of radius 5.08 cm and length 15.24 cm constructed of copper was fabricated, and this contained the sample for examination. The cylinder had a brass, water-tight flange at one end and a type K thermocouple was mounted in the flange in such a way that when the vessel was assembled the tip of the thermocouple was at the centre of the cylinder. The thermocouple lead passed to a hybrid recorder.

The thermal diffusivity is itself a function of temperature so in order to measure it, it is necessary to take a fairly small range of heating or cooling.

Materials

Three Thai coals and one Australian (Morwell, Victoria) coal were used in this study. their proximate analysis figures (weight percentages) are given below in Table 1.

The Thai samples were prepared for use by means of a jaw crusher affording particle sizes in the range 6 to 15 mm which gave the required densities.

TABLE 1

Proximate analyses

Coal	Volatile matter (%)	Moisture (%)	Fixed C (%)	Ash (%)	
Thai coal #1[a]	28.7	17.9	12.7	40.7	Extremely high in ash
Thai coal #2[a]	32.5	28.7	28.3	10.5	
Thai coal #3[a]	32.3	35.7	23.0	9.0	Relatively high-grade coal
Victorian coal[b]	48.3	–	48.7	3.0	Run-of-mine coal

[a]As-received basis, analysis performed as part of the program described.
[b]Dry basis, analysis data provided by the donors of the coal sample (State Electricity Commission of Victoria).

Results and discussion

(i) Reactivity measurements

Central to the concepts underlying the measurement of activation energies by the method chosen is the phenomenon of criticality: behaviour such that a very small difference in the *ambient* temperature of an exothermically reacting mass leads to fundamentally different types of thermal behaviour. This is very clearly demonstrated in Fig. 1, which shows temperature–time trajectories for Thai coal 2, such trajectories being plotted from the thermocouple signals. At an ambient temperature of 427 K, the behaviour is subcritical; the temperature at the centre of the sample rises to only a small excess above ambient before dropping, presumably because of oxygen depletion in the region of the thermocouple. On the other hand, at an ambient temperature of 431 K—a mere 4 K higher—ignition results, and the temperature reaches values in excess of 700 K. Hence the critical ambient temperature for an ignition of this coal, in this size of basket at the density employed, can reliably be stated as 429 ± 2 K. Criticality was this unequivocal for all of the materials examined at all of the basket sizes used.

The data were plotted according to eqn. (1), and values of the activation energy of ignition obtained from the slopes. Figures 2(a) to 2(c) show such plots for the three Thai coals. Linearity is clear, and in each case the activation energy was calculated from the line fitted to the points. Table 2, below, gives a summary of the results for the Thai coals and also for the Victorian coal studied for comparison. Also included are values previously obtained by the same method for other low-rank coal samples.
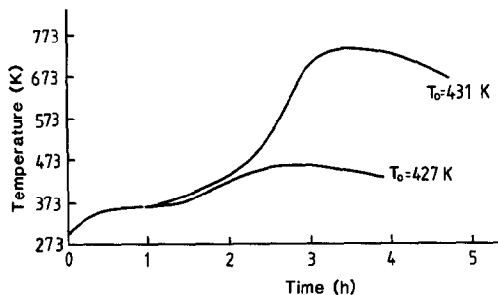
Fig. 1. Sub- and supercritical temperature-time trajectories for Thai coal #2 in a basket of 4 cm side at the density indicated in Table 2.
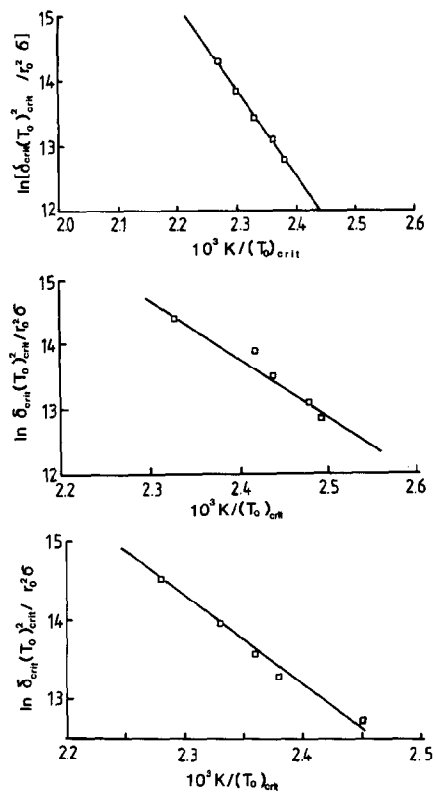

Fig. 2. Frank–Kamenetskii plots for (a) Thai coal #1, (b) Thai coal #2, and (c) Thai coal #3.

From error analysis of the points in Figs. 2(a) to 2(c), the uncertainties in the activation energies are believed not to exceed a few percent.

Prior to consideration of the respective E_a values, theory and experiment can be checked for consistency by examination of the temperature excess of

the subcritical trajectory in Fig. 1, found to be 34 K. Theory [6, 12] predicts that this temperature is:

$$T_{max} - (T_0)_{crit} = 1.866 \frac{R(T_0)^2_{crit}}{E_a}$$

$$= \text{maximum temperature excess for stability}$$

Substituting $(T_0)_{crit} = 429$ K (from Fig. 1) and $E_a = 75$ kJ mol^{-1} (from Table 2) gives a maximum temperature excess of 38 K, in satisfactory agreement with the measured 34 K.

Plots 2(a) to 2(c) were obtained using densities of sample in the various sizes of basket not varying by more than a few percent (see Table 2). It was found that attempts to use densities differing widely gave rise to considerable scatter of the points. This is unusual, as in some materials so examined differences in density can be accommodated in eqn. (1) by inserting appropriate values in the argument of the logarithm. This involves the implicit assumption that the effective thermal conductivity does not vary significantly with density, and this appears not to hold for the Thai coals examined. It is likely that this is due to the high mineral and inorganic content of the coals, reflected in the high ash contents.

Values of the activation energy of ignition of the order of 10^2 kJ mol^{-1} for the coals examined are consistent with those reported for comparable materials as shown in the table and also with values for humic and carbonaceous materials [5]. The spread observed is of interest, and appears to be shared by the material type which is the geological precursor of coals, namely vegetation. The present group [13] have observed similar spreads in activation energies of ignition of vegetation litter, believed on the basis of comparisons with in-

TABLE 2

Activation energies of ignition of low-rank coals

Material	σ (kg m^{-3})	E_a (kJ mol^{-1})	Reference
Thai coal #1	765	111	Present work
Thai coal #2	658 ± 30	75	Present work
Thai coal #3	634 ± 22	95	Present work
Victorian coal	530 ± 30	94	Present work
New Zealand lignite	510 to 670	88	[11]
Victorian briquette fragments[a]	460 to 560	89	[12]

[a]Manufactured from Yallourn coal, differing from the Victorian coal used in the present work, which is Morwell run-of-mine coal having experienced no compaction or binding process.

dependent work [14] to be attributable to the differing contributions of cellulose, hemicellulose and lignin. Factors possibly influencing reactivity of coals include maceral content and porosity, relevant to intrinsic reactivity and oxygen contact respectively, and scope for further work in correlating these properties with reactivity is indicated by our results.

(ii) Heat transfer

Figure 3 shows heating and cooling curves for a sample of Thai coal 2, and the expected symmetry is apparent. Thermal diffusivities calculated in the manner described in Appendix 1 are listed in Table 3 below, and the table includes values for other types of material for comparison. The values of α obtained in the present work are the mean of values from heating and cooling curves. Discrepancies between the two are in each case very small, as are errors inherent in the technique. Uncertainties in the values of α are therefore believed not to exceed 3%.

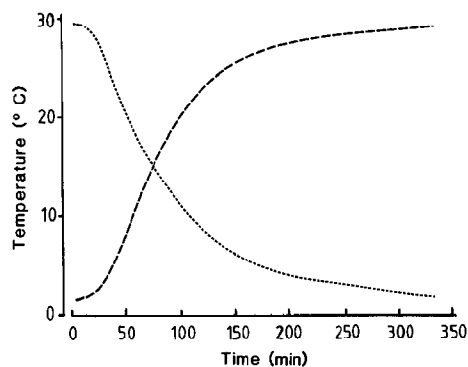It is of interest to record for each of the above the product of thermal diffu-

Fig. 3. Heating and cooling curves for Thai coal #2 at the density indicated in Table 3.

TABLE 3

Thermal diffusivities

Material	σ (kg m^{-3})	$10^6 \alpha$ (m^2 s^{-1})	Reference
Thai coal #1	791	0.142	Present work
Thai coal #2	631	0.113	Present work
Thai coal #3	735	0.119	Present work
Victorian coal	524	0.113	Present work
Dead vegetation	121	0.290	[10]
Commercial char[a]	616	0.275	[9]

[a]Prepared from Yallourn, Victorian coal.

TABLE 4

Products of diffusivity and bulk density

Material	$\alpha\sigma$ $(\text{kg m}^{-1}\text{s}^{-1})$
Thai coal #1	112
Thai coal #2	71
Thai coal #3	87
Victorian coal	59
Dead vegetation	35
Commercial char	169

sivity and bulk density ($\alpha\sigma$, units kg m^{-1} s^{-1}). This is constant for a single material the thermal conductivity and heat capacity of which do not vary with density. The materials above represent a range *loosely* mirroring coalification: from dead vegetation through 'immature' coals to material very high in carbon. Table 4 gives the values of $\alpha\sigma$.

The indication from the limited data available is that processes reflecting geological advance along the coalification series (increase in carbon, decrease in oxygen) are accompanied by increases in $\alpha\sigma$. The very low value for the wood, the high value for the char and intermediate values for the four low-rank coals support this tentative view.

Conclusions

The low-rank coals examined show clearly critical behaviour under the conditions realised by the experiments described, conditions believed scientifically to represent industrial scale stockpiling and transportation realities. One limitation of the type of experiment described in the work concerned with reactivity is that certain secondary factors are not simulated. Such secondary factors include heat of wetting effects and creation of reactive (unweathered) surface by breakage. However, the primary factor in coal stockpile instability is unquestionably oxidation by atmospheric oxygen, and this occurrence is put on to a firm basis for predictive or modelling purpose by measurements of the type described. The role of the secondary factors is to exacerbate the primary oxidation effect.

The other crucial factor in thermal stability—heat transfer—has also been put on to a quantitative basis, and the values of the thermal diffusivity presented are suitable for input to numerical simulations of stockpile behaviour.

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Appendix I

Calculation of α from the heating and cooling curves

When a cylindrical sample of radius a is transferred from a bath at temperature T_0 to another at temperature T_∞, the temperature at the centre of the cylinder changes according to the equation:

$$\frac{T(t) - T_0}{T_\infty - T_0} = 1 - \frac{8}{\pi} \sum_{n=0}^{\infty} \sum_{m=1}^{\infty} \frac{(-1)^n \exp(-\alpha t/a^2)\,[q_m^2 + \{(2n+1)(\pi a^2/2)\}]}{(2n+1)q_m J_1(q_m)}$$

$$(\text{I.1})$$

where J_0 are Bessel functions of order zero, and q_m are the roots of $J_0(q_m) = 0$. The dimensionless quantity on the left of eqn. (I.1) is a normalised temperature, and by means of a computer program a plot can be generated of this normalised temperature versus the dimensionless group $\alpha t/a^2$. The plot is for a particular value of half-height to radius ratio, chosen as 1.5 in the present work.
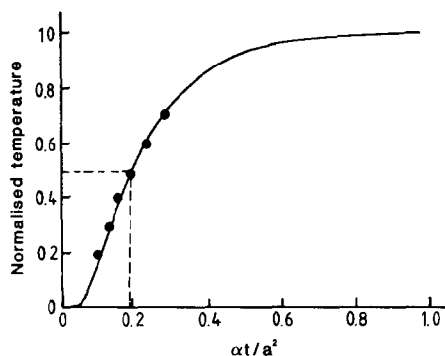
Fig. I.1. Comparison of theoretical (eqn. I.1) and experimental points on the normalised temperature versus $\alpha t/a^2$ (Fourier number) curve. Continuous curve: theoretical. Filled circles: experimental points.

Measurement of α from a heating or cooling curve (Fig. 3) involves measuring the time for the sample to reach normalised temperature 0.5 and substituting the time in the corresponding value of $\alpha t/a^2$, from which a value for α is obtainable. The method is therefore a single-point determination, the validity of which can be checked by obtaining experimental values of $\alpha t/a^2$ on the basis of the measured values of α, and comparing those at various times with the computer-generated theoretical values. Figure I.1 shows such a check for one of the materials (the Victorian coal); the continuous line is the theoretical one and the points are experimental. The agreement is seen to be extremely close.

Notation

a	Radius of cylinder, m
α	Thermal diffusivity, $\text{m}^2\,\text{s}^{-1}$
σ	Bulk density, kg m^{-3}
δ_{crit}	Frank–Kamenetskii parameter
A	Pre-exponential factor, s^{-1}
c	Heat capacity, $\text{J kg}^{-1}\,\text{K}^{-1}$
E_{a}	Activation energy of ignition, kJ mol^{-1}
q	Heat of reaction, kJ kg^{-1}
k	Thermal conductivity, $\text{W m}^{-1}\,\text{K}^{-1}$
l	Cylinder half-length
r_0	Frank–Kamenetskii radius, m
R	Gas constant (8.314), $\text{J K}^{-1}\,\text{mol}^{-1}$
t	Heating or cooling time, s
$T(t)$	Temperature as a function of t, K
T_0	Ambient (oven) temperature (reactivity experiments), K
T_0	Bath temperature (heat transfer experiments), K
T_∞	Second bath temperature (heat transfer experiments), K