

COAL: KINETIC ANALYSIS OF THERMOGRAVIMETRIC DATA *

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ABSTRACT

Thermogravimetry, TG, is widely used to investigate rate processes. This method involves the continuous measurement of the change in mass or rate of mass loss, DTG, of a sample with temperature (or time). Such data has been used to determine kinetic parameters, such as activation energy and order of reaction. A number of methods have been developed in the literature to permit kinetic analysis of TG data. The kinetic parameters for the decomposition of coal are frequently calculated from one TG curve obtained at a constant heating rate. Since kinetic parameters are influenced by the heating rate, methods involving one thermogram have been criticized on the basis that they may give incorrect values for the activation energy and reaction order, and that only methods involving multiple heating rates will give reliable results. In this work, comparison is made of four methods for analyzing TG data of a sub-bituminous coal.

NOMENCLATURE

A	pre-exponential factor in the Arrhenius equation
C	conversion $1 - [(m - m_f)/(m_i - m_f)]$
C_z	conversion at z relative to complete coal devolatilization in air (z located at minimum mass-loss rate between zones II and III)
C_f	overall conversion relative to complete coal-devolatilization in air
E	activation energy, kJ mole^{-1}
\bar{E}_{II}	a weighted average E corresponding to decomposition zone II, kJ mole^{-1} (individual activation energies were calculated assuming $n = 1$)
\bar{E}_{III}	a weighted average E corresponding to decomposition zone III, kJ mole^{-1} (individual activation energies were calculated assuming $n = 1$)
\bar{E}_{ov}	a weighted overall E based on E_{II} and E_{III} , kJ mole^{-1}
E_{II}	average E corresponding to decomposition zone II (data fitted to one equation) kJ mole^{-1}
E_{ov}	average corresponding to total decomposition range (data fitted to one equation), kJ mole^{-1}
k	rate constant in Arrhenius equation, min^{-1}
m	mass at T , mg

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m_f	mass at T_f , mg
m_i	mass at T_i , mg
$-dm/dt$	rate of mass loss, mg min^{-1}
n	order of reaction, dimensionless
n_{II}	order of reaction corresponding to decomposition zone II
n_{ov}	overall order of reaction
R	ideal gas constant, $9.31 \text{ J mole}^{-1} \text{ K}^{-1}$
S	shape index ratio of tangents of inflection at the increasing and decreasing part of a rate curve
T	temperature, K
T_{max}	temperature at maximum rate of mass loss, K
TC	temperatures were corrected
TNC	temperatures were not corrected
dT/dt	heating rate, $^{\circ}\text{C min}^{-1}$
ΔT	temperature difference between sample and furnace thermocouples
t	time, min

INTRODUCTION

This work was prompted by a conclusion reached by Flynn and Wall [1] in their review of methods used for thermogravimetric analysis, TG. They maintained that methods involving one heating rate (or thermogram) would give unreliable values of the activation energy, except where the decomposition of the material occurs "by the same simple kinetic process". As a rule, only methods involving multiple heating rates will give meaningful results [1].

This study is an evaluation of a number of methods used to study the decomposition of coal [2,3] and wood [4], in order to determine the extent of variation between activation energy values obtained by methods using a single heating rate, on the one hand, and those obtained by methods involving several heating rates, on the other. A sub-bituminous coal will be used throughout.

EXPERIMENTAL

The coal was a sub-bituminous coal used in previous studies [5,6]. Pyrolysis of the coal was performed in a duPont 951 thermogravimetric analyzer, which recorded the mass loss (TG) and rate of mass loss (DTG) against temperature (or time) in the range 293–1223 K. The heating rate and flow rate of nitrogen (dry) were maintained respectively at $20^{\circ}\text{C min}^{-1}$ and 50 ml min^{-1} at stp. The coal mass was 15 mg.

BASIC THEORY

The decomposition of coal may be represented by the rate equation [5,8]

$$\frac{dC}{dt} = k(1 - C)^n \quad (1)$$

where C is the conversion, k is the specific rate constant and n is the reaction order. The conversion may be defined in terms of m_1 , the initial mass of coal (moisture-free basis), m , the mass at time t , and m_f , the mass at the end of the experiment, by the equation

$$C = 1 - \frac{m - m_f}{m_1 - m_f} \quad (2)$$

Assuming that the specific rate constant, k , varies with temperature according to the Arrhenius equation, viz.

$$k = A \exp\left(-\frac{E}{RT}\right) \quad (3)$$

and combining eqns. (1), (2) and (3), we obtain

$$-\frac{dm/dt}{m_1 - m_f} = A \exp\left(-\frac{E}{RT}\right) \left[\frac{m - m_f}{m_1 - m_f}\right]^n \quad (4)$$

Equation 4 is widely used for calculating kinetic data such as activation energy, E , from TG curves [2,5-8].

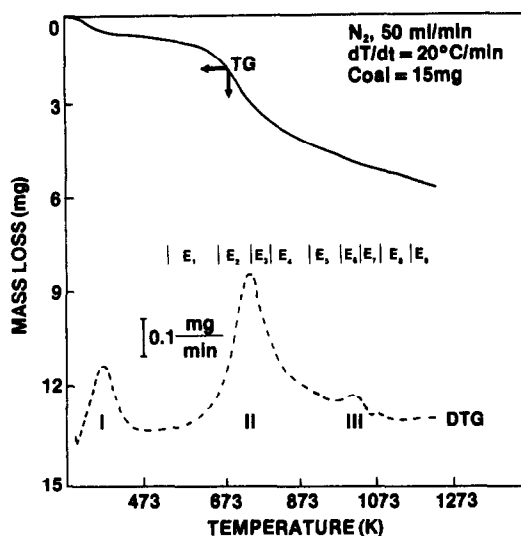


Fig. 1 Thermogravimetric heating curve for coal in nitrogen (10^5 N m^{-2}).

CALCULATION OF KINETIC PARAMETERS

A number of methods using single and multiple heating rates will be presented.

Method 1A

This is the most widely used method to calculate the activation energy of coal in TG. It entails the use of eqn. (5) which is obtained by taking the logarithm of eqn. (4).

$$\log_{10} \frac{-dm/dt}{m_i - m_f} \left[\frac{m_i - m_f}{m - m_f} \right]^n = \log_{10} A - \frac{E}{2.3RT} \quad (5)$$

When n is assumed to be unity in accordance with Van Krevlin [2], then a plot of the left-hand side of eqn. (5) vs. $1/T$ will result in a number of straight lines corresponding to different temperature regions along the thermogram, see Fig. 1. An activation energy may subsequently be obtained from the slope ($-E/RT$) of each line. In Fig. 2, two (out of nine) such lines are shown for coal decomposed in a nitrogen atmosphere. Values of E corresponding to ranges 1, 3 and 8 are shown in Table 1. \bar{E}_{II} , \bar{E}_{III} and \bar{E}_{ov} are weighted activation energies ($J \text{ mole}^{-1}$) for regions II, III and the overall

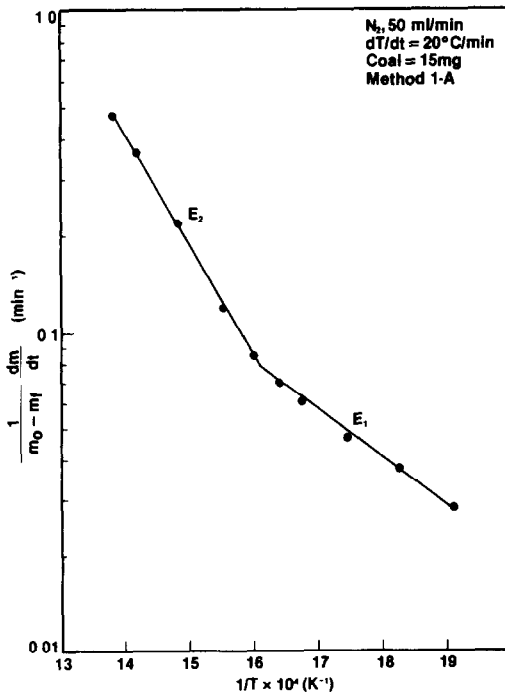


Fig 2 Rate of reaction of coal in nitrogen (10^5 N m^{-2})

TABLE 1

Effect of temperature correction on activation energy (Method 1)

Activation energy	TNC		TC	
	Temperature range (K)	E (kJ mole ⁻¹)	Temperature range (K)	E (kJ mole ⁻¹)
E_1	523–618	27.9 ± 1.2	523–608	30.0 ± 1.5
E_3	723–823	50.2 ± 2.5	705–802	49.1 ± 2.4
E_8	1123–1223	43.8 ± 2.8	1108–1208	42.6 ± 2.7
\bar{E}_{II}	523–938	50.9 ± 2.3	523–915	50.4 ± 1.9
\bar{E}_{III}	938–1223	67.2 ± 4.5	915–1208	65.9 ± 4.7
\bar{E}_{OV}	523–1223	55.0 ± 4.6	523–1208	56.0 ± 4.8

reaction, respectively. The equation used was

$$\bar{E} = E_1 \Delta C_1 + E_2 \Delta C_2 + \dots + E_n \Delta C_n \quad (6)$$

where ΔC in this case is the fraction converted in moles corresponding to a temperature range, ΔT , at which the activation energy was operative. However, using ΔC in terms of mass resulted in an insignificant change in the

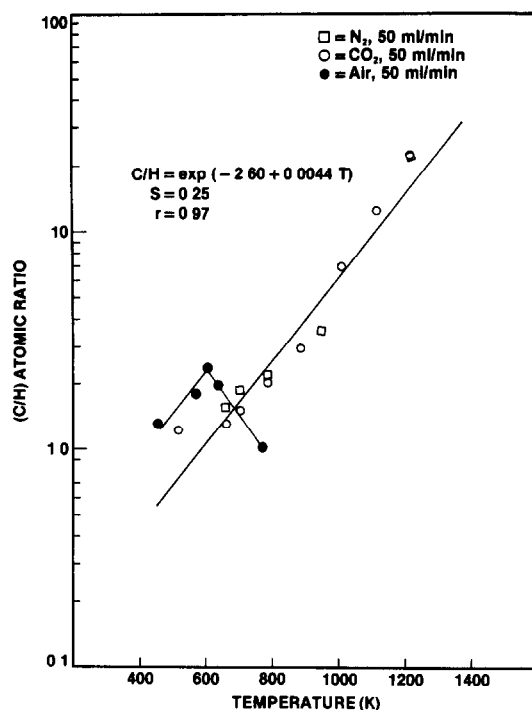


Fig. 3. Change of coal (C/H) atomic ratio with temperature in nitrogen, air and carbon dioxide.

TABLE 2

Average activation energy using Method 1A

Activation energy	Mole fraction (kJ mole ⁻¹)	Mass fraction (kJ mole ⁻¹)
\bar{E}_{II}	50.9 ± 2.3	50.2 ± 2.1
\bar{E}_{III}	67.2 ± 4.5	64.6 ± 4.5
\bar{E}_{ov}	55.0 ± 4.6	56.0 ± 4.6

value of the activation energy, see Table 2. To convert the mass change in a given temperature interval into moles, values of the C/H atomic ratio shown in Fig. 3 were used. The temperature ranges within which the respective activation energies are operative are also indicated in Table 1.

Method 1B

A weighted average activation energy may be obtained by fitting the experimental points corresponding to the left-hand side, LHS, or right-hand side, RHS, of a decomposition zone, e.g. zone II, using eqn. (5). Such values of E are shown in Fig. 4 plotted against the corresponding experimental pre-exponential factor (A). In this case, n was not assumed to be unity, as in Method 1A, but was varied from 0 to 2.0. On the basis of the square of the correlation coefficient, r^2 , only the LHS of the decomposition range (zone II) was well represented by $n = 1$. On the other hand, for the LHS, the higher value of r^2 ($= 0.99$) was obtained when n was chosen as zero.

Method 1C

To determine an overall order of reaction for zone II, the data was fitted to a least-squares equation. The results are shown in Fig. 5 for different

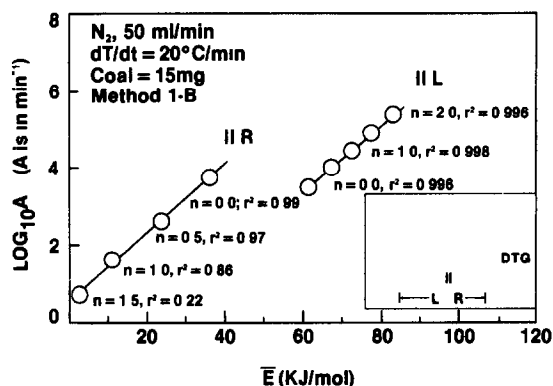


Fig 4 Effect of reaction order on kinetic parameters

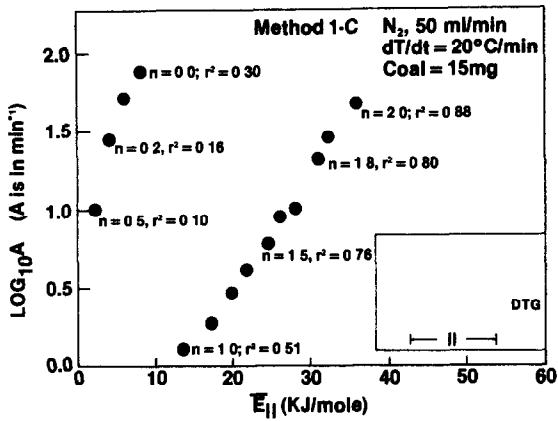


Fig. 5 Effect of reaction order on kinetic parameters.

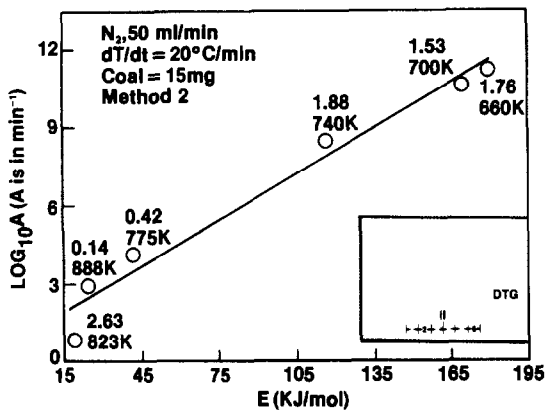


Fig. 6 Variation of kinetic parameters along the thermogram

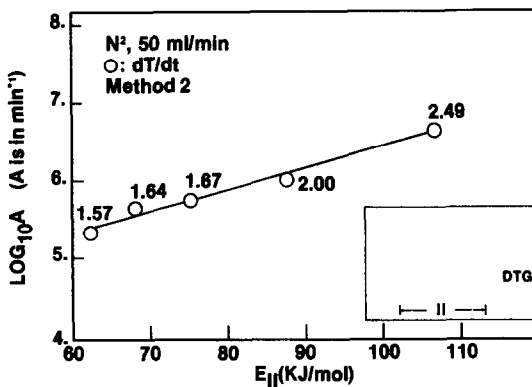


Fig. 7. Effect of operating parameters on kinetic parameters in zone II

assumed values of n . It is apparent that coal decomposition in zone II cannot be represented by a first-order reaction as was suggested [2]. When n was assumed to be unity, $r^2 \approx 0.51$. In order that $r^2 = 1$, the value of n must be chosen to be greater than two.

Method 2

Duvvuri et al. [9], in their study on the pyrolysis of cellulose, showed that the order of reaction may be obtained experimentally by rewriting eqn. (5), such that

$$y = a + bx + cz \quad (7)$$

where $a = \log_{10} A$, $b = E/2.3R$, $c = n$, $z = \log_{10}[(m_1 - m_f)/(m - m_f)]$, and $y = [\log_{10}(1/(m_1 - m_f))(-dm/dt)]$.

Equation 7 was used to calculate the kinetic parameters at different points along the thermogram shown in Fig. 1. The results for the six positions investigated along zone II are given in Fig. 6. (Each position corresponds to one temperature.) An interesting feature is that the order of reaction which varied from 0.14 to 2.63 was not related to the absolute temperature or change in activation energy. The variation of E and $\log_{10} A$ indicates a positive "kinetic compensation effect". This point will not be discussed here and is the subject of a separate report [10].

Figure 7 shows the change in E , $\log A$ and n for zone II with heating rate (5, 10, 20, 50 and 100°C min⁻¹). Each point was obtained by fitting the data for the respective zone II to eqn. (7) using the least-squares method. The results show that the order of reaction increased from 1.57 to 2.49 with variation in heating rate from 5 to 100°C min⁻¹. The same trend was observed when the overall range of decomposition was considered, see Fig. 8.

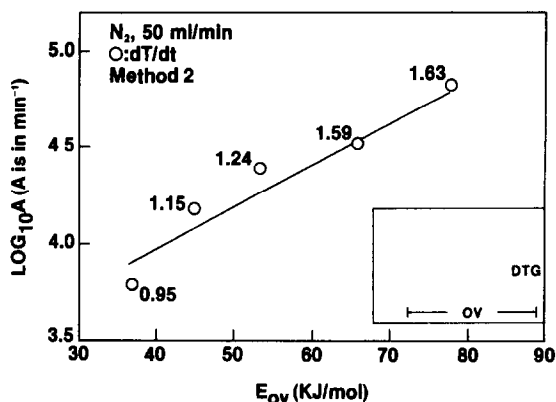


Fig. 8. Effect of operating parameters on overall kinetic parameters

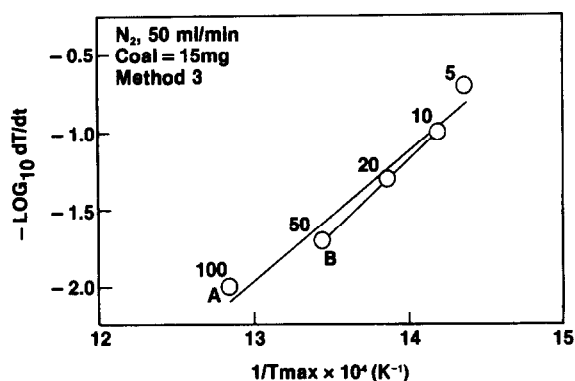


Fig. 9 Effect of heating rate combination on activation energy

Method 3

Van Krevlin [2] proposed an equation to obtain the activation energy, given by

$$-\log \frac{dT}{dt} = A + \frac{E + 2RT_{\text{inf}}}{2.3RT_{\text{max}}} \quad (8)$$

where T_{inf} and T_{max} are, respectively, the temperature at the inflection point and that at which the rate of volatilization is maximum. The quantity $2RT_{\text{inf}}$ is less than 2 kJ mole^{-1} and may be neglected. Therefore, a plot of $-\log_{10} dT/dt$ vs. $1/T_{\text{max}}$ at different heating rates should provide a value from the slope ($-E/2.3T_{\text{max}}$): such lines are shown in Fig. 9 for two heating rate combinations. The activation energy for combination B (10, 20 and $50^{\circ}\text{C min}^{-1}$) was greater than for combination A (5, 10, 20, 50 and $100^{\circ}\text{C min}^{-1}$). Table 3 shows the variation of the activation energy for other heating rate combinations.

TABLE 3

Influence of heating rate combination on activation energy (Method 3)

Combi- nations	Heating rates	TNC		TC	
		$E \text{ (kJ mole}^{-1}\text{)}$	r^2	$E \text{ (kJ mole}^{-1}\text{)}$	r^2
A	5, 10, 20, 50, 100	146.2 ± 17.9	0.950	146.2 ± 18.7	0.950
B	10, 20, 50	163.1 ± 3.9	0.999	163.4 ± 5.9	0.998
C	20, 50, 100	115.3 ± 23.8	0.930	115.0 ± 24.8	0.930
D	5, 10, 20	205.7 ± 44.6	0.920	206.2 ± 50.8	0.900
E	5, 20, 100	144.8 ± 23.0	0.955	145.9 ± 24.0	0.950

Method 4

In a recent study dealing with the effects of catalysts on the kinetic parameters of the decomposition of wood, Trans and Rai [4] calculated the activation energy at selected conversions using a method which involved several rates of heating. In this case, eqn. (5) rather than (7) was used. Their results indicated that for the decomposition of wood, the activation energy increased linearly with conversion for 60% of the range of conversion. The results for coal decomposition obtained in this study using this method are shown in Figs. 10 and 11 and clearly indicate that only when a temperature correction, TC, is applied should this method be used. A linear fit to the data when no temperature correction, TNC, was applied, produced a very low correlation as indicated by the values of r^2 in Fig. 11. The change in activation with conversion is only linear during the initial decomposition stage (less than 10% conversion) after which a cyclical pattern is followed, Fig. 12.

Temperature corrections

During the analysis of a coal sample, there exists a temperature difference between the sample and furnace thermocouple. Since the thermal decomposition of this coal in nitrogen is exothermic, the sample temperature will always be higher than that of the furnace at any one instant. A method to

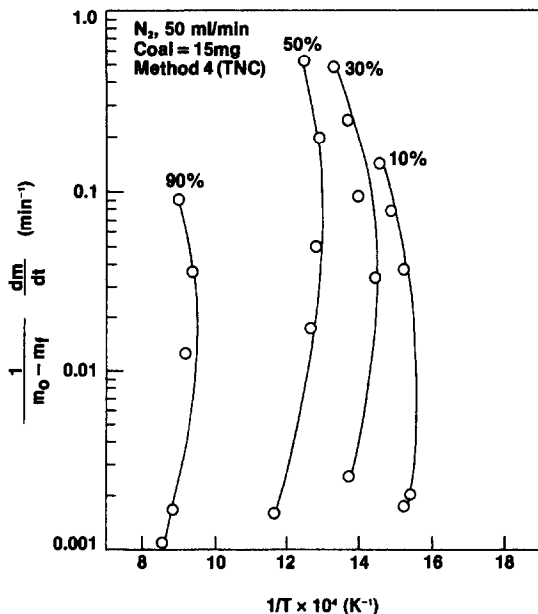


Fig. 10. Plots to determine activation energy of coal at various conversion levels

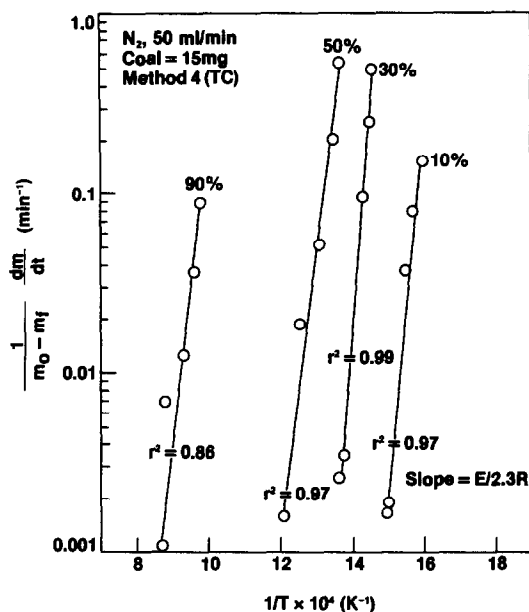


Fig 11. Plots to determine activation energy of coal at various conversion levels.

correct for this effect is given in Appendix I in accordance with ref. 6. The temperature correction is applied to rectify the error resulting from the difference between the temperature of the sample thermocouple and that measuring the furnace thermocouple.

Of the four methods compared, the two involving one heating rate did not require corrections to be made for the difference between the sample and the furnace temperatures. This may be deduced in the case of Methods 1 from Table 1. Further confirmation was obtained by testing for the degree of dispersion between TC and TNC values of E using the Chi-square test. This

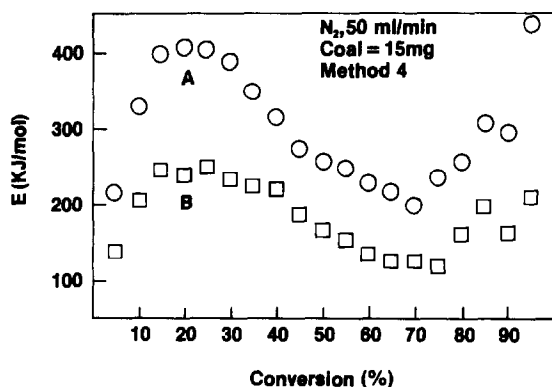


Fig. 12 Effect of heating rate combination on activation energy along the thermogram.

gave $\chi^2 (0.49) < \chi_{7,0.05}^2 (2.17)$, which indicates that the precision of the two columns of data investigated was the same. Similar results were obtained for Method 2 and are not shown here. It is interesting to note that, unlike Method 4, Method 3, which involves multiple heating rates, required no temperature correction (Table 3). This can be explained by the effect of heating rate on the procedural temperatures. For example, the increase in heating rate from 5 to 100°C min⁻¹ increased both the initial decomposition temperature and T_{\max} linearly [6]. On the other hand, the total amount of coal decomposed in a nitrogen atmosphere decreased with heating rate in a non-linear way within the temperature range studied (298–1223 K). This was mainly due to a reduction in the mass decomposed in the degasification stage (zone III). What happened, in effect, was a shift of the reactions towards higher temperatures as well as an increase in the temperature range of reaction [6].

DISCUSSION

A comparison of the values of the kinetic parameters calculated using the different methods investigated here, indicates a large disparity in values. For example, when Method 1A was used, the value of E along the thermogram varies between 25 and 70 kJ mole⁻¹ (Table 1). However, values as high as 400 kJ mole⁻¹ were calculated using Method 4 which involves several rates of heating, see Fig. 12. Values of E obtained using Method 3 are within 100–200 kJ mole⁻¹ depending on the heating rate combination, see Table 3.

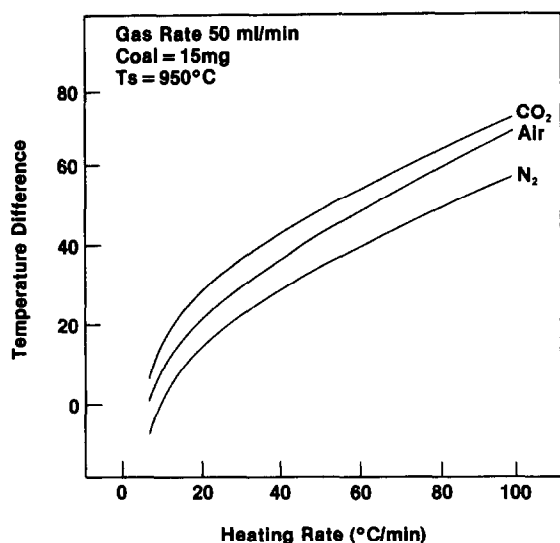


Fig 13 Effect of heating rate on the temperature difference between the sample and furnace temperature

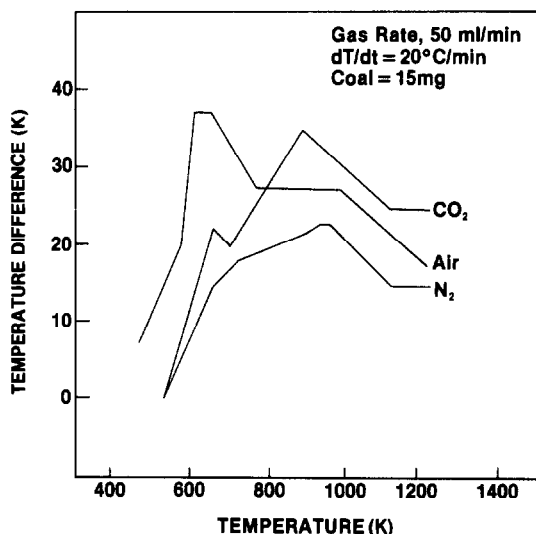


Fig 14 Effect of furnace atmosphere on the temperature difference between the sample and furnace thermocouples

It is apparent that methods involving multiple heating rates give values of the activation energy which are dependent on the heating rate combination. This may be due to the fact that the amount of coal converted is not linearly related to the rate of heating [6]. This suggests that data obtained using a given combination of multiple heating rates should only be compared to that obtained using the same heating rate combination. In a previous study [6], the activation energy and order of reaction using Methods 1 or 2 were shown to be linearly related to the shape factor, S , which is a measure of the dissymmetry of a zone of reaction [11]. When such plots have been built for a range of experimental conditions they may be used to calculate an activation energy from the shape factor measured off the thermogram under other conditions. This is an attractive feature of the methods requiring one heating rate, over and above the fact that they do not require any temperature correction, which is a time consuming process.

CONCLUSIONS

- (1) Methods 1A and 2 are recommended for thermogravimetric analysis of coal.
- (2) Methods in which several heating rates are used give values of the activation energy and pre-exponential factor which are dependent on the heating rate combination.
- (3) The activation energy and T_{\max} both increase linearly with heating rate.

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APPENDIX I Sample calculations

If the set temperature was 800 K and the heating rate was $100^{\circ}\text{C min}^{-1}$, the corrected temperature in an atmosphere of nitrogen may be obtained as described.

- (1) Read the value of ΔT at $100^{\circ}\text{C min}^{-1}$ from Fig. 13, $(\Delta T)_{100} = 56^{\circ}$.
- (2) Read the value of ΔT at $20^{\circ}\text{C min}^{-1}$ from Fig. 13, $(\Delta T)_{20} = 13^{\circ}$
- (3) Subtract (2) from (1), i.e. $56^{\circ} - 13^{\circ} = 43^{\circ}$
- (4) Read the value of $(\Delta T)_{20}$ at 800 K, from Fig. 14. This is equal to 19°
- (5) Add (3) and (4), i.e. $19 + 43 = 62$
- (6) Subtract (5) from the set temperature. the corrected temperature = 738 K