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KINETICS OF THE THERMAL DECOMPOSITION OF ANIMAL BONE CHAR

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ABSTRACT

The effect of process variables, i.e. initial surface area and rate of heating, on the production of carbon-free bone ash, as well as its technique, were investigated. Thermogravimetric analysis up to 1000°C indicated that a uniform rate of heating of 10°C $\min^{-1}$ was more favourable than 5°C $\min^{-1}$. Also, grinding to achieve 180 and 98 m^2 g^{-1} surface area for the bone char and bone char waste accelerated the combustion process. Dynamic heat treatment resulted in a deflection in the activation energy where below 400°C it was 4.75 kcal $mole^{-1}$ and only 2.07 kcal $mole^{-1}$ was obtained between 400 and 700°C. Isothermal heat treatment yielded an activation energy of 4.07 kcal $mole^{-1}$ for both samples.

INTRODUCTION

The kinetic study of the thermal decomposition of solids depends mainly on the following factors: (i) initial and final temperature of decomposition; (ii) the rate of temperature increase; (iii) the atmosphere surrounding the solid sample (inert, oxidizing or reducing); and (iv) the nature or state of the solid sample itself (size of particles). These factors, in general, greatly affect the texture, structure and composition of the final product.

In dealing with kinetic data, it should be taken into consideration that the overall rate of a complex process involving a series of consecutive steps is fixed by the rate of the slowest single step. The one with the lowest energy barrier will be the most rapid, major contributor to the overall process [1].

The kinetics of the thermal decomposition of solids are usually studied by measuring the fraction α of material reacted at constant temperature T and pressure P [2]. Another method of analysis is where the residual weight fraction is related to the temperature for a sample heated at a fixed rate [3].

In a previous publication [4], the thermal decomposition of animal bone carbon and bone carbon waste was investigated in air and in vacuum. It was found that thermal treatment yielded a direct change in the surface area which was accompanied by changes in the amount of chemisorbed water.

The present work is devoted to a study of the kinetics of the thermal

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treatment of bone char and bone char waste. A knowledge of the kinetics of such changes accompanying the decomposition is essential in determining its practical feasibility.

EXPERIMENTAL

Materials

Samples of animal bone char(Ad) and its waste(Adw) after the refining process of sugar were supplied by the Sugar Refining Co., Hawamdya, Egypt, for the present study.

Grinding and surface area

Both samples were ground in an automatic agate mortar for 40 min. The specific surface areas of the two samples, as provided and after grinding, were measured using the BET method and N_2 as adsorbate.

Thermogravimetric analysis

The samples were heated continuously at a constant rate while the loss in weight was recorded. The rate of heating was varied between 5 and 10°C min^{-1} to determine the correct rate. An automatic thermobalance, provided by Gebrüder Netzsch, W. Germany, was used.

Dynamic heat treatment

Known weights of the specimens were heated in porcelain crucibles in an electric upright muffle from room temperature to the required temperature at a rate of 10°C min^{-1}. The specimens were taken out of the kiln at temperatures in the range 200–700°C after various soaking times of 4, 7, 10, 60, 120, 180 and 240 min. Experiments were carried out in duplicate.

Isothermal heat treatment

A known weight of each sample was inserted in the muffle at temperatures in the range 450–650°C with 50°C intervals. The specimens were withdrawn from the muffle after a given time. Prior to the isothermal experiments all the specimens were fired in a platinum dish at a rate of 10°C min^{-1} up to 400°C for 10 min and immediately allowed to cool in a desiccator.

RESULTS AND DISCUSSION

Surface area

The BET surface areas of the two samples as provided by the manufacturer (Ad and Adw) and after grinding (Adg and Adwg) are:

	Ad	Adg	Adw	Adwg
S.S.A. ($m^2 g^{-1}$)	*112*	*180*	*66*	*98*

The differences in the final values of S.S.A. of both samples, although similar weights of the samples were ground with the same speed for a fixed time, are attributed primarily to the differences in the starting surface areas and the nature of each sample.

Effect of grinding on the burning process

The DTG curves of both samples heated continuously and uniformly at a rate of 10°C min^{-1} are illustrated in Fig. 1 (A and B) for the Ad and Adw

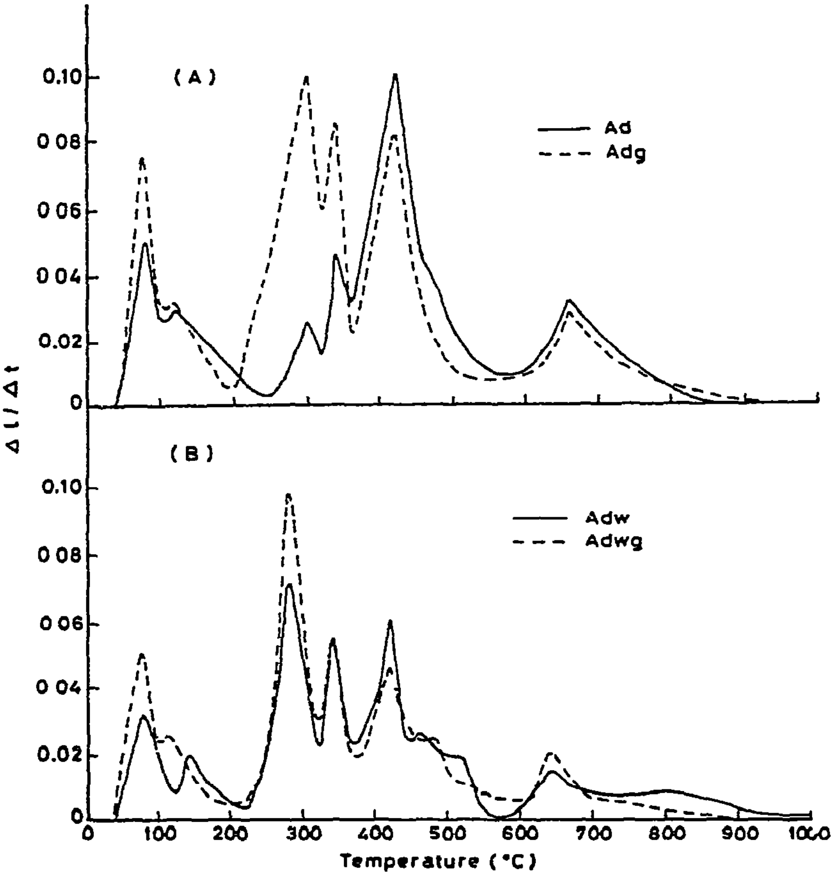

Fig. 1. Differential weight losses for both samples before and after grinding. Heating rate. 10°C min^{-1}.

samples, respectively, before and after grinding. The ground samples have comparatively higher weight loss values below 340°C. These correspond to the dehydration, dehydroxylation and decarbonization. The recorded loss in both samples is unexpectedly lower upon grinding. This means that part of the carbon has already been oxidized at lower temperatures. The same behaviour is observed for the peak recorded at 660°C which is attributed to the release of volatiles. The curves are characterized by many peaks denoting the separation of the individual reaction steps.

Additional thermogravimetric analysis of both samples, as received and when ground, was carried out but at a slower rate, i.e. 5°C min^{-1} [Fig. 2 (A and B)]. A clear distinction is observed between the curves in Figs. 1 and 2. The latter is characterized by three peaks occurring only at 80, 360 and 620–660°C. The first two are due to dehydration, dehydroxylation and decarbonization, while the latter could be attributed to volatiles. Generally,

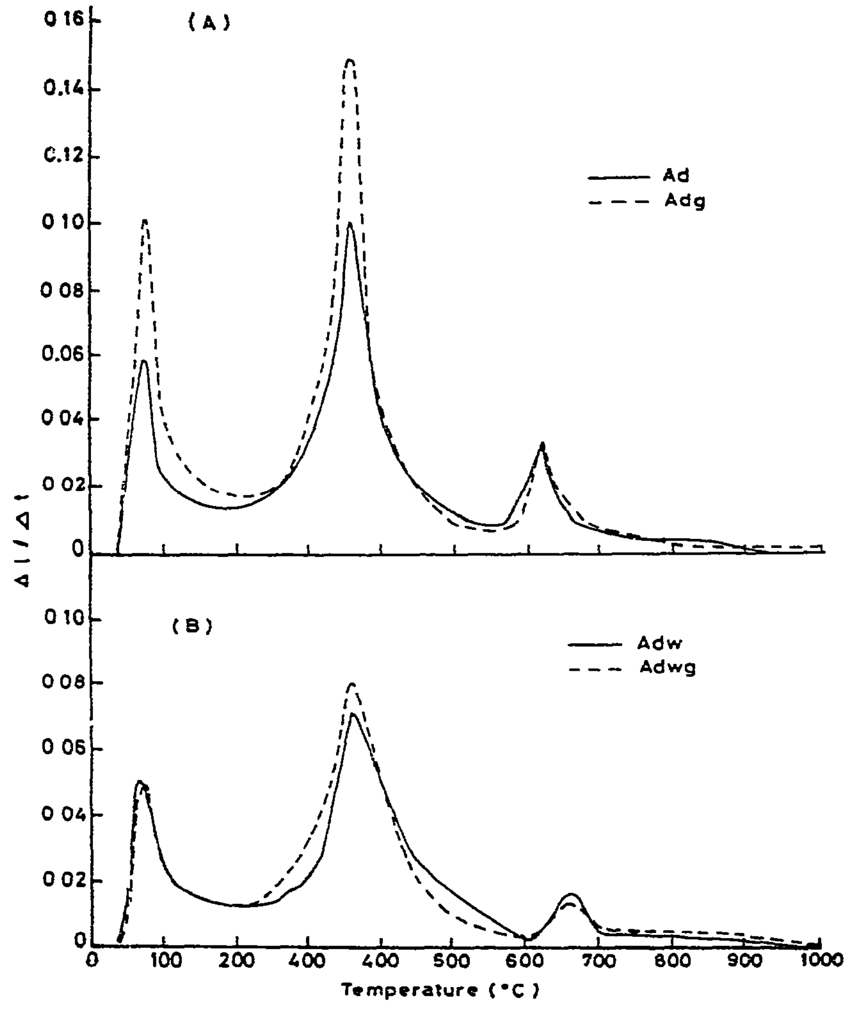

Fig. 2 Differential weight losses for both samples after grinding Heating rate. 5°C min^{-1}.

the grinding process affected much more weight loss, especially for the bone char sample (Ad).

It is clear that the grinding process promoted the reactions through the newly formed active surfaces. This activation is related to the stored energy in the ground material as well as the smaller particle size. Upon grinding, the existing bonds in the material are broken, a process that leads to an increase in its internal energy. The increase in free energy per unit area of the newly formed surface is known as the surface energy [1]. Consequently the present promoted reactions are attributed to the driving force provided by the excess free energy of the newly increased surface. In this connection, the particle size is equally important as the rate of many reactions is inversely proportional to the particle size.

Effect of rate of heating

Comparing the data plotted in Figs. 1 and 2 for the continuous uniform rates of heating of 10 and 5°C min^{-1}, respectively, it is found that the former rate allows the reactions to proceed through more than one step, independent of initial particle size, for both samples. The areas under the peaks are larger in the case of the high temperature gradient, i.e. 10°C min^{-1}, which proves that the slower rate of 5°C min^{-1} allowed partial fixation of carbon.

Dynamic heat treatment

In this technique the samples were subjected to a stepwise increase of temperature, at a uniform heating rate, for various periods of time. The weight loss data are given in Table 1. The relative weight changes, R $(\alpha_{\text{time}}/\alpha_{10\text{min}})$, are also included.

Plots of R against temperature for both samples (Fig. 3) show that R relations are higher for the Adg sample. High values of R are obtained when the samples are held for longer time periods at low temperatures. Above 400°C longer incremental times produced similar weight changes irrespective of the temperature, i.e. the rate of loss is slowed down. Plots of residual fraction $\ln(1-\alpha)$ against time (t) at different temperatures (Figs. 4 and 5) gave straight lines in the region up to 10 min (Fig. 6). From these straight lines, the rate constant (k) was determined at each temperature. A plot of log k vs. the reciprocal of absolute temperature ($1/T$) gave satisfactory straight lines with two slopes (Fig. 7). The activation energies are calculated from these curves using the Arrhenius equation

$$\mathrm{d}\ln k/\mathrm{d}T = E/RT^2$$

$$\left(\ln k = \frac{-E}{RT} + \text{const}\right)$$

TABLE 1

The loss extent after different times relative to loss extent after 10 min by dynamic treatment

Temp. (°C)	Fraction reacted (α)				Relative weight change (R)		
	10 min	120 min	240 min	300 min	R_1 120/10	R_2 240/10	R_3 300/10
Adg sample							
200	0.029	0.049	0.057	0.059	1.720	1.965	2.030
300	0.060	0.099	0.118	0.119	1.665	1.996	1.983
400	0.111	0.153	0.157	0.158	1.381	1.417	1.426
500	0.129	0.164	0.166	0.167	1.271	1.287	1.294
600	0.161	0.179	0.180	0.180	1.114	1.121	1.121
700	0.174	0.180	0.183	0.184	1.034	1.034	1.054
Adwg Sample							
200	0.021	0.029	0.034	0.034	1.409	1.651	1.661
300	0.056	0.077	0.084	0.089	1.377	1.500	1.553
400	0.098	0.122	0.124	0.125	1.340	1.265	1.276
500	0.120	0.139	0.139	0.139	1.154	1.158	1.162
600	0.129	0.142	0.144	0.144	1.096	1.112	1.112
700	0.145	0.149	0.149	0.149	1.025	1.032	1.034

where T is the absolute temperature and E is the activation energy.

It is interesting to note that in both samples the reactions proceeded via the same mechanism. On heating below 400°C a higher activation energy is obtained, i.e. 4.75 kcal mole^{-1}. Above 400°C, the activation energy is only

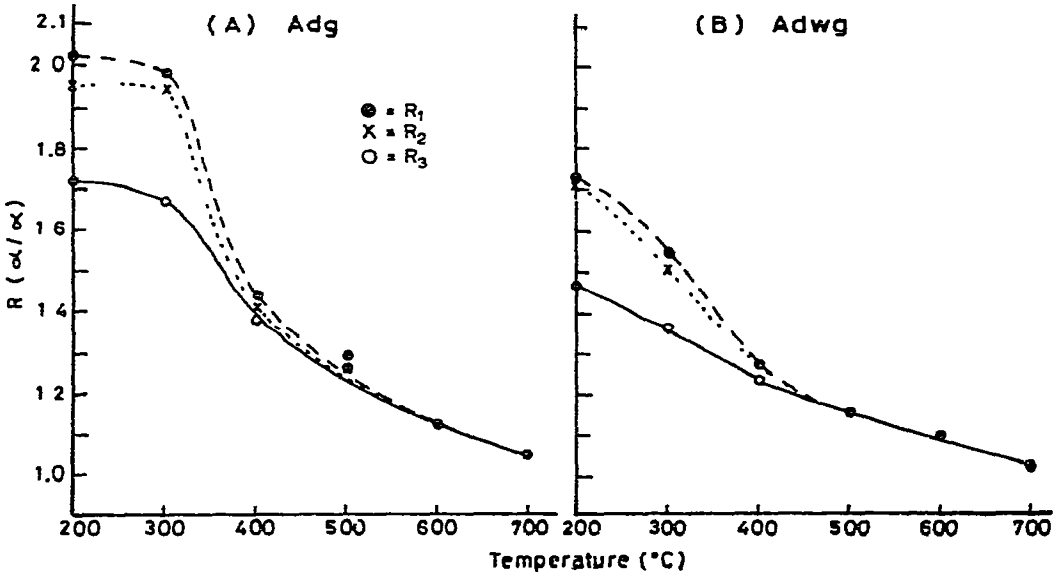

Fig 3. Relative loss extent vs. temperature for A=Adg and B=Adwg samples after dynamic treatment.

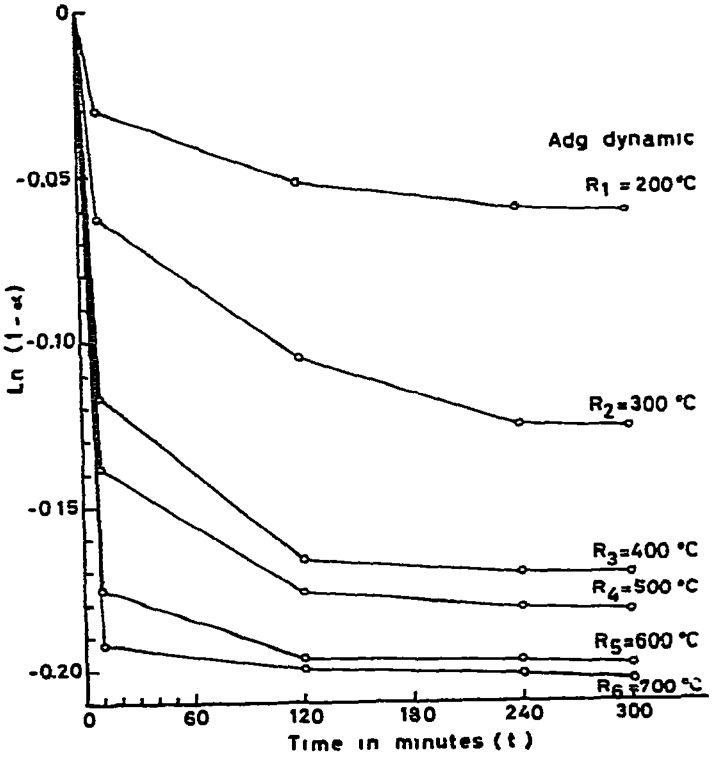

Fig. 4. Relation between ln(1 − α) vs. time of the dynamic treatment at different temperatures for the Adg sample.

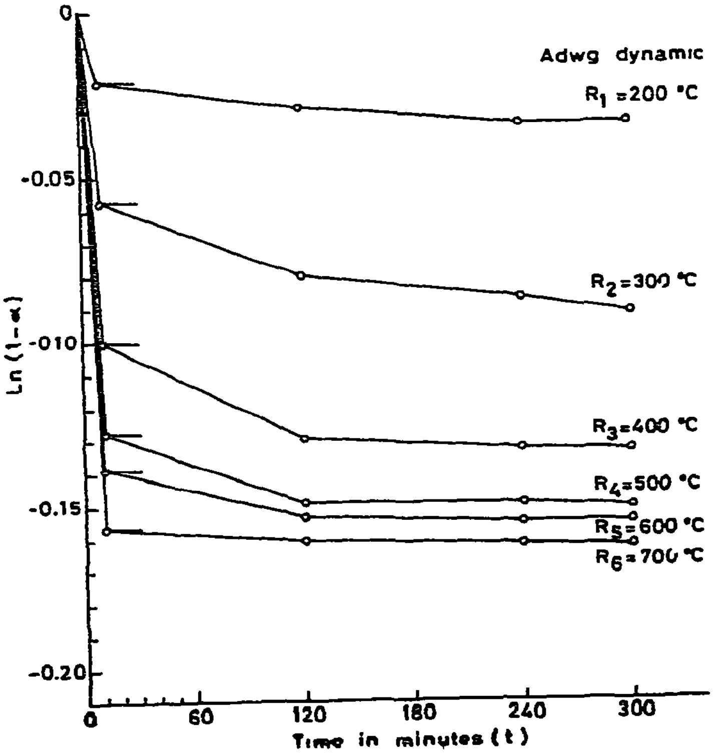

Fig. 5. Relation between ln(1 − α) vs. time of the dynamic treatment at different temperatures for the Adwg sample.

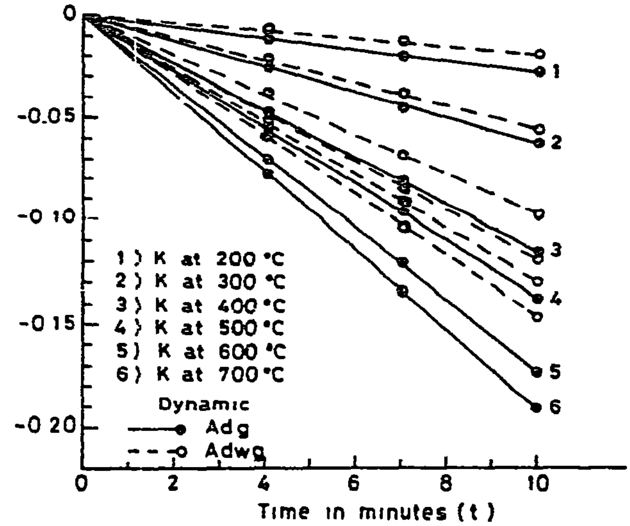

Fig. 6 $\ln(1-\alpha)$ vs. time (up to 10 min) of dynamic treatment at different temperatures for Adg and Adwg samples.

2.06 kcal $mole^{-1}$. Two such different energies are obtained for the superimposed reactions being dehydration, dehydroxylation and decarbonization This proves that the transport mechanism has actually changed. In the present system the heterogeneous reactions occurring are obviously controlled by two classes of rate controllers. The nucleation reaction has been shown to be controlled by the phase boundary rate while the oxidation reaction is controlled by the transport rate [1]. The exothermic peak previously recorded for the oxidation of carbon at 380 and 410°C for Adw and Ad samples [4] means that the process is controlled by heat flow where the

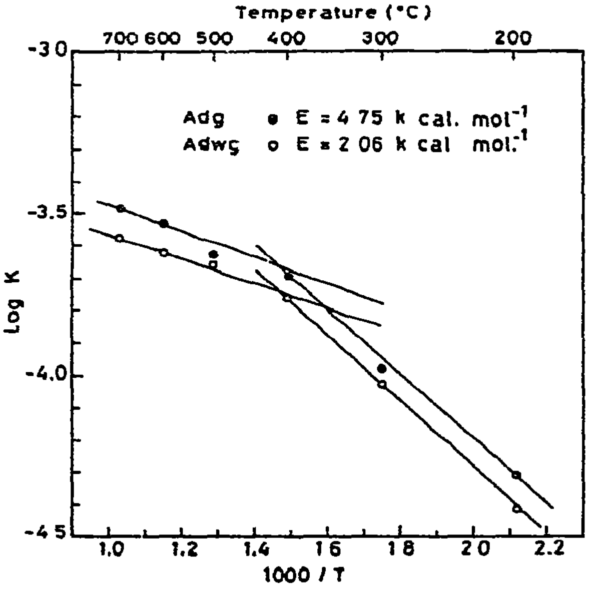

Fig. 7. Activation energy of both samples calculated from the relation between log k vs. $1/T$.

heat evolved tends to raise the interface temperature. This may explain the lower activation energy value obtained above 400°C.

Isothermal heat treatment

In this method the preheated samples were kept for certain lengths of time at constant temperatures and the weight changes were noted. The samples were preheated and quenched at 400°C at a rate of 10°C min^{-1} for 10 min. This temperature proved to be a deflection temperature at which the activation energy of the reaction changed upon dynamic heat treatment. The loss extent (α) as well as the relative weight changes (R) are given in Table 2.

Plotting the relative weight changes (R) against temperature (Fig. 8) illustrates higher R at the lower temperatures experienced, being higher for the Adwg sample. The relative weight changes apparently proceeds to a state where further increase in temperature does not cause a substantial decrease in weight. This is to be expected since it has been shown that as the temperature difference between experiment temperature and equilibrium temperature decreases, the diffusion coefficient and driving force decrease for dehydration and decomposition reactions [1,5].

Plots of residual fraction $\ln(1-\alpha)$ vs. time (t) for the various temperatures are illustrated in Fig. 9 (A and B) for the Adg and Adwg samples. This Fig. exhibits behaviour similar to the dynamic heat treatment in that the fraction remaining after 120 min does not change much with higher incremental times. Also, the first 10 min yielded the highest change. Plots of

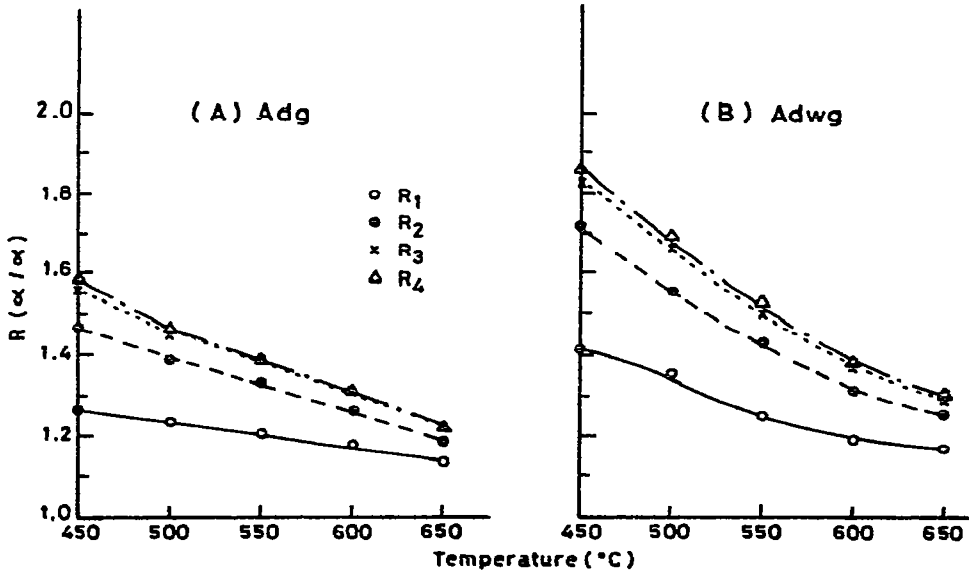

Fig. 8. Relative loss extent vs. temperature for A = Adg and B = Adwg samples after isothermal treatment.

TABLE 2

The loss extent after different times relative to loss extent after 10 minutes by isothermal treatment

Temp. (°C)	Fraction reacted (α)					Relative weight change (R)			
	10 min	60 min	120 min	180 min	240 min	R_1 60/10	R_2 120/10	R_3 180/10	R_4 240/10
Adg sample[a]									
450	0.042	0.053	0.062	0.065	0.066	1.26	1.47	1.55	1.56
500	0.049	0.060	0.068	0.071	0.072	1.24	1.39	1.46	1.46
550	0.056	0.068	0.075	0.078	0.078	1.22	1.34	1.39	1.39
600	0.059	0.070	0.075	0.078	0.078	1.18	1.26	1.30	1.30
650	0.087	0.097	0.103	0.104	0.106	1.12	1.19	1.20	1.22
Adwg sample[b]									
450	0.026	0.037	0.044	0.048	0.049	1.41	1.70	1.83	1.86
500	0.031	0.042	0.048	0.051	0.052	1.36	1.56	1.66	1.69
550	0.036	0.045	0.052	0.054	0.055	1.25	1.44	1.50	1.53
600	0.042	0.051	0.056	0.058	0.059	1.19	1.32	1.39	1.39
650	0.047	0.055	0.059	0.061	0.069	1.17	1.26	1.30	1.31

[a] Dynamic treatment at 400°C (0.1108).

[b] Dynamic treatment at 400°C (0.098).

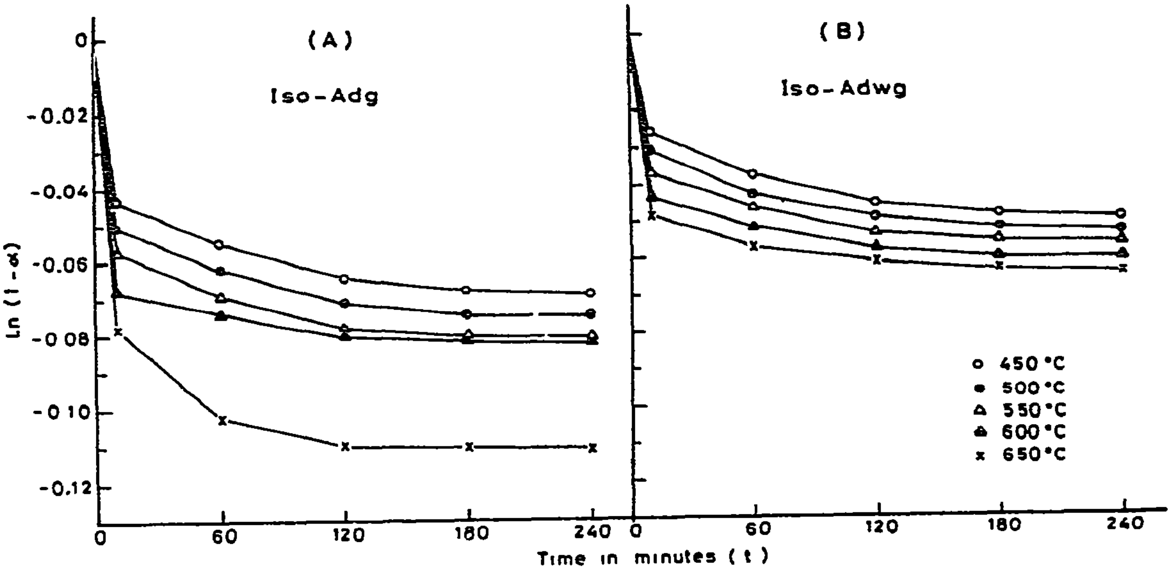

Fig. 9 Relation between $\ln(1-\alpha)$ vs. time of isothermal treatment at different temperatures for A=Adg and B=Adwg samples

$\ln(1-\alpha)$ vs. (t) for the first 10 min, at various temperatures, gave the rate constants (Fig. 10A and B). The activation energies are obtained by plotting the rate constants (k) vs. the reciprocal of the absolute temperature $(1/T)$

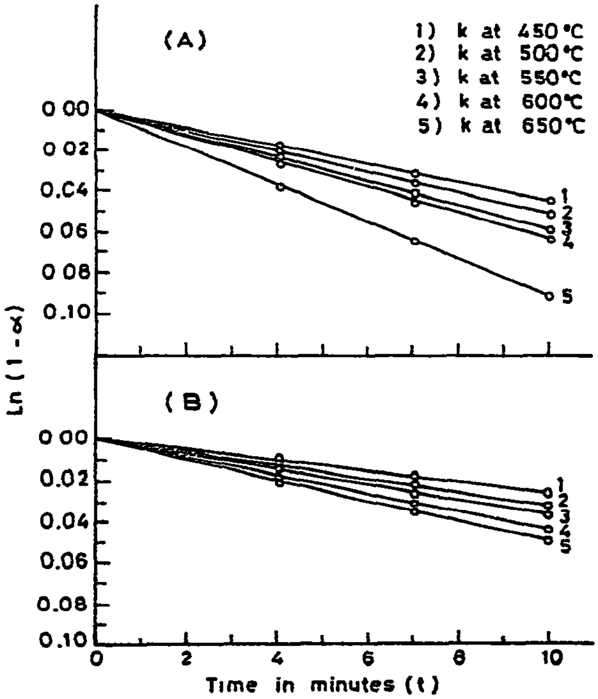

Fig. 10. $\ln(1-\alpha)$ vs. time (up to 10 min) of isothermal treatment at different temperatures for A=Adg and B=Adwg samples.

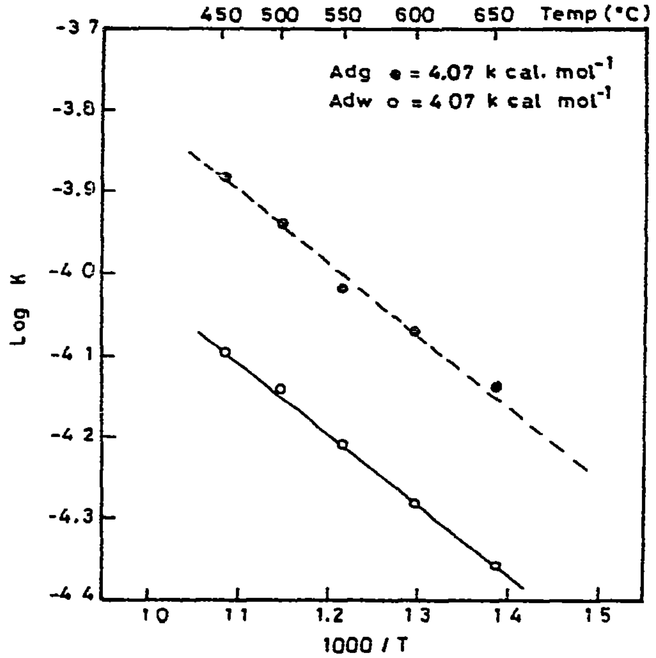

Fig 11. Activation energy of both samples calculated from the relation between log k vs. $1/T$.

(Fig. 11). Both samples gave nearly the same activation energy, indicating that material transport proceeded via one and the same mechanism.

Comparing the activation energies recorded for the isothermal and dynamic heat treatments at temperatures above 400°C (4.07 and 2.06 kcal mole^{-1}, respectively) reflects the different conditions of the two procedures. The lower activation energy in the case of the dynamic treatment is attributed to the gradual proceeding of the reactions rather than the isothermal one having its rate dependent on diffusion. The greater activation energy of the isothermal treatment means greater sensitivity to thermal changes [6].

CONCLUSIONS

Grinding of both samples accelerated the burning process due to the smaller particle size and newly active exposed surface for reactions.

The continuous uniform rate of heating of 10°C min^{-1} was found to be more favourable, as undesirable fixation of carbon occurred with the rate of 5°C min^{-1} as tested thermogravimetrically.

The loss extent increased with increasing the time of treatment at low temperatures, i.e. <400°C. At higher temperatures it was independent of time.

In the dynamic thermal treatment, the reactions proceeded via the same mechanism for the two samples with 4.75 kcal mole^{-1} up to 400°C and 2.06 kcal mole^{-1} from 400 to 700°C.

The reactions in the case of isothermal treatment also proceeded via the same mechanism with an activation energy of ≈ 4 kcal mole^{-1}.

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