

THERMOGRAVIMETRIC INVESTIGATION OF THE CARBONIZATION OF SOME PITCHES

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Introduction and method of analysis

The technique of non-isothermal thermogravimetry is a standard method of assessing the pyrolysis range of organic materials and can, in favourable circumstances, be used to obtain kinetic parameters. However, in this latter application it should be used with caution since differences in kinetic parameters can arise where methods of interpretation vary (1). These methods have been critically reviewed by Sharp (1) and Doyle (2) and the application to the pyrolysis of pitches and similar materials is briefly discussed here before being applied to a thermogravimetric study of selected samples.

The kinetics of isothermal decomposition reactions are described by the general rate equation,

$$\frac{d\alpha}{dt} = A \cdot f(\alpha) \cdot \exp\left(-\frac{E}{RT}\right) \quad \dots [1]$$

where α is the fractional weight loss, $f(\alpha)$ takes a form dependent on the mechanism of the reaction and the other terms have their usual meanings. Under dynamic conditions [1] becomes

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \cdot f(\alpha) \cdot \exp\left(-\frac{E}{RT}\right) \quad \dots [2]$$

where β is the constant heating rate. Equation [2] can be used either in its differential or integrated form and there are a diversity of methods of evaluating the integral. In pyrolysis reactions of concern here $f(\alpha)$ has usually been assumed to take the form

$$f(\alpha) = (1 - \alpha)^n \quad \dots [3]$$

where n is supposedly an 'order' of reaction (3), (5) often having a value between 1 and 2. However, as Sharp (1) points out only certain values of n have any physical significance for heterogeneous reactions. Moreover, the $f(\alpha)$ may not be the same over the whole pyrolysis range especially in the case of pitches which are extremely fluid when volatilization commences but become semi-cokes as α tends to unity.

Wallouch, Marty and Heintz (4) combined equations [2] and [3] and evaluated the temperature coefficients of pyrolysis of a variety of pitches, which varied from 40-100 kJ mole⁻¹. Hutterer (5) used [2] and [3] in integral form, evaluating the integral by van Krevelen's referent method (3) and also obtained apparent activation energies in the above range. However, much higher values (250-350 kJ mole⁻¹) were measured by Lapina et al (6) for precursors which yield graphitizable products. These results can be compared with van Krevelen's (1) own studies of coals and related materials which yield values of about 200 kJ mole⁻¹.

Since van Krevelen's studies other approximations to the integral form of equation [2] have been proposed (2) and a particularly useful expression is

$$\log g(\alpha) = \log\left(\frac{AE}{\beta R}\right) - a - \frac{bE}{RT} \quad \dots [4]$$

where $g(\alpha)$ is the integral of $f(\alpha)$ and a and b are empirical constants which are tabulated by Doyle (2) and can be used to evaluate E from a suitable plot of the thermogravimetric data. Ozawa (7) has suggested a very simple method of determining kinetic parameters based on equation [4] in which the thermo-

gravimetric data is determined at a number of constant heating rates and E is determined from

$$\left(\frac{d \log \beta}{d\left(\frac{1}{T}\right)}\right)_\alpha = -\frac{bE}{R} \quad \dots [5]$$

since $\log g(\alpha)$ is constant at constant values of α . This method has advantages for reactions such as pitch pyrolyses since no assumption need be made about the kinetic mechanism and the activation energy can be determined at different values of α regardless of whether the same $f(\alpha)$ applies at all stages of the process. However, it is assumed that the $f(\alpha)$ does not change with temperature at a fixed value of α . Friedman (8) has suggested a similar method based on equation [2] in which

$$\ln \left(\beta \cdot \frac{d\alpha}{dT}\right)_\alpha = \ln A + \ln f(\alpha) - \frac{E}{RT} \quad \dots [6]$$

although this method should be less accurate since it involves differentiation of the thermogravimetry curve.

In this study these two methods have been applied to the pyrolysis of selected pitches.

Experimental

100 mg samples of pitch were suspended in open silica crucibles from one arm of a CI Electronics Mark 2B microbalance and heated at a constant rate in a continuous flow of dry nitrogen at a flow rate of 50 mls min⁻¹. The furnace was controlled by a Stanton Redcroft linear programmer capable of rates between 0.5 and 10°C min⁻¹. The temperature was monitored immediately below the sample crucible and displayed continuously along with the weight change on an Oxford 2000 2-pen chart recorder.

The materials investigated were an Orgreave coal tar binder pitch (softening point, 101°C, Ring and Ball), an Orgreave coal tar impregnation pitch (softening point, 83°C, Ring and Ball); Gilsonite pitch and an Ashland petroleum pitch (200).

Results and Discussion

The normalised α -temperature curves are shown in Fig.1 for the Orgreave binder pitch and the applications of Ozawa and Friedman's methods of analysis are illustrated in Figs 2 and 3. The slopes in both these cases increase with increasing values of α indicating that the activation energy changes with the fractional weight loss. A similar effect occurs with the other materials and the activation energies are given in Table 1.

Table 1

Sample	Activation Energies	
	Ozawa method (kJ mole ⁻¹)	Friedman method (kJ mole ⁻¹)
Orgreave binder pitch	78-140	78-165
Orgreave impregnation pitch	66-110	70-110
Ashland 200	135-160	150-160
Gilsonite	115-160	-

The two methods of analysis give remarkably similar results although Ozawa's method is much the simpler to apply and is therefore to be preferred. The range of activation energies for each sample increases with the softening point consistent with the observations of Wallouch *et al* (4). These authors also observed that mixing two pitches of different softening points resulted in an activation energy for pyrolysis intermediate between those of the two starting materials. In view of the results in this study their activation energies should perhaps be considered to represent average values over the pyrolysis range. However, they serve to emphasise that pitches are mixtures of complex organic molecules with varying molecular weight distributions. During pyrolysis, polymerisation processes and distillation of low molecular weight fragments shift the distribution towards higher molecular weights and the carbonaceous mesophase separates out eventually as a separate phase. Hence, in view of the dependence of the activation energy on softening point, which is also related to the molecular weight distribution, it is perhaps not too surprising to find that the activation energy for pyrolysis increases with fractional weight loss.

References

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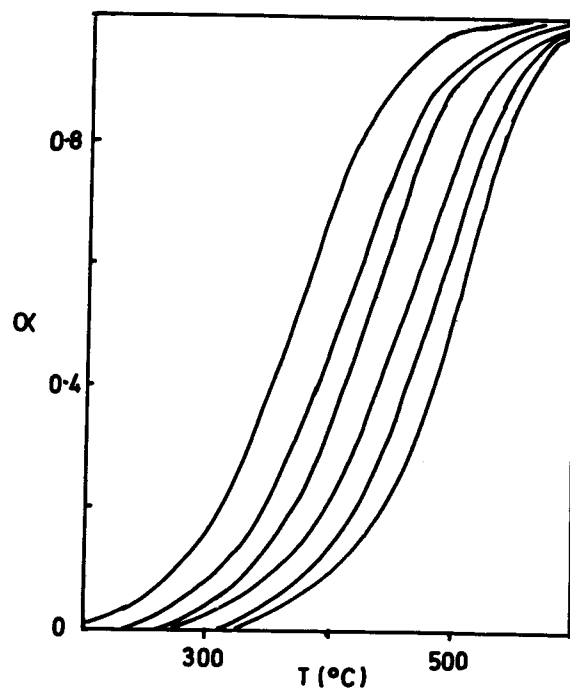


Fig.1 TG curves for binder pitch at different heating rates

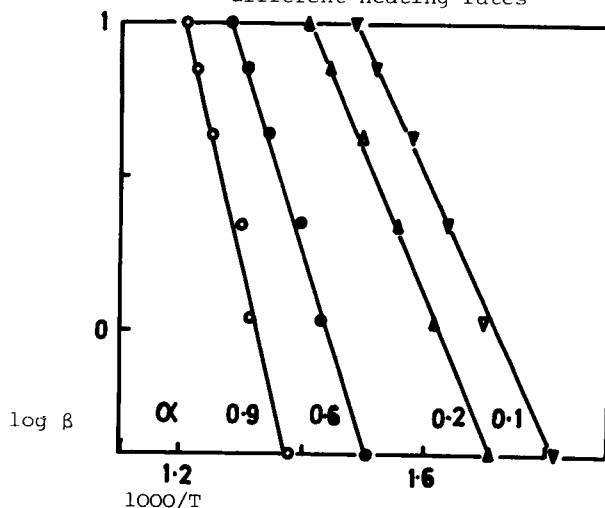


Fig.2 Ozawa plot of data in Fig.1

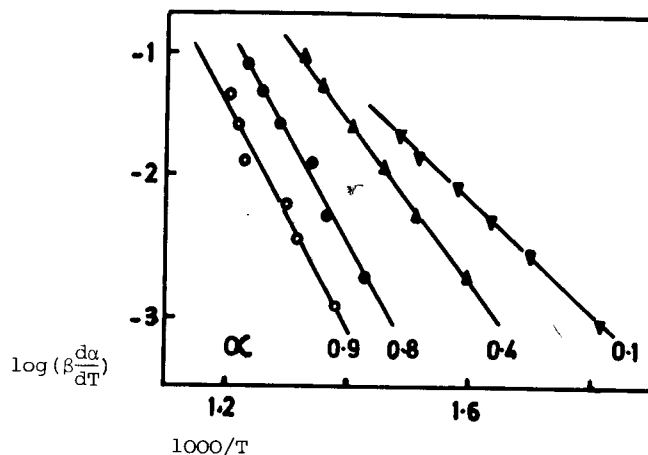


Fig.3 Friedman plot of data in Fig.1