

## Determination of the relative oxidative stability of petroleum bitumens by thermogravimetry

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### Abstract

An isothermal thermogravimetric technique was used to determine the apparent activation energies ( $E_a$ ) for the oxidative degradation of petroleum bitumens produced from different crude sources and with different histories. The values of  $E_a$  were found to be different for each bitumen. For a particular bitumen,  $E_a$  was independent of temperature over the range studied (240–370°C), but increased with increasing fractional conversion ( $\alpha$ ). A good correlation at low  $\alpha$  was established between  $E_a$  and the durability value for each bitumen. The durability value is a relative measure of oxidative stability derived from an oven aging procedure (100°C) which has been found to be useful in predicting actual sprayed bitumen seal lifetimes in the field.

### INTRODUCTION

The in-service age hardening of petroleum bitumens used in road construction leads, over 10–20 years, to embrittlement of the binder and a consequent deterioration in the road surface. Experience has shown that bitumens produced from different crude sources can have very different durability properties, and a means of predicting these properties becomes of prime importance in order to screen out unsatisfactory materials.

The major cause of age hardening in the field is atmospheric oxidation; a number of other features are also thought to contribute to the effect but to a much lesser extent [1]. In the laboratory, age hardening is often modelled by measuring viscosity changes after oven oxidation of thin bitumen films [2], or by the use of high pressure oxygen at near-ambient temperatures [3]. One such procedure (the Australian durability oven test [4]) is an attempt to model the long-term field aging of bitumens used in sprayed seal surfacings. Dickinson [5] and Oliver [6] have developed a model involving

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the laboratory determined durability value and climatic parameters which enables successful prediction of approximate seal lifetimes [6]

$$\log \eta = 0.0476TY^{0.5} - 0.0227DY^{0.5} + 3.59$$

where  $\eta$  is the true viscosity (Pa s) of the bitumen recovered from the seal,  $Y$  is the number of years since the seal was constructed,  $D$  is the durability oven test value, and  $T$  is the average temperature of the site calculated from  $T = (T_{\max} + T_{\min})/2$ , where  $T_{\min}$  and  $T_{\max}$  are the yearly means of the daily maximum and minimum air temperatures respectively.

Thus for a given locality the rate of age hardening is proportional to the laboratory determined durability value.

The procedure used to determine  $D$  is, however, very time consuming, often taking two weeks to a month. In the present work, thermogravimetry (TG) was investigated as a rapid means of establishing relative oxidative stabilities for a number of different bitumens. As non-isothermal TG curves were found to be only poorly reproducible, an isothermal kinetic analysis was carried out, and apparent activation energies ( $E_a$ ) were determined. These values were then correlated with data from the durability oven aging procedure to establish the relevance of the high temperature TG data to field aging.

## EXPERIMENTAL

### *Samples*

The bitumens chosen for study were constituted in different ways and from a number of different crudes, giving a range of durability properties. All bitumens were 180/200 penetration grade and had similar physical properties (Table 1).

### *Thermal analysis*

Experiments were carried out on a Mettler TG50 thermobalance controlled by a Mettler TC10A processor. The raw data were transferred to a computer for analysis. Bitumen samples (9.8–10.2 mg) were analysed in an open platinum crucible (5 mm high, 5 mm inner diameter) in air or nitrogen as purge gas (200 cm<sup>3</sup> min<sup>-1</sup>). Inorganic ash contents of the bitumens were negligible (less than 0.1% w/w) and were ignored in the subsequent data treatment.

### *Oven aging*

Laboratory aging of the bitumens was carried out according to the Australian durability oven procedure [4]. This consists of the rolling thin

TABLE 1  
Physical properties<sup>a</sup> and constitution of the studied bitumens

Bitumen	Crude composition	Blend <sup>b</sup> composition	Density at 25°C	Penetration at 25°C: 100 g, 5 s (0.1 mm)	Softening point (°C)	Viscosity at 70°C (mm <sup>2</sup> s <sup>-1</sup> )	Viscosity at 135°C (mm <sup>2</sup> s <sup>-1</sup> )	Flash point (°C)
A	Safaniya 100%	100% SR	1.020	186	38.8	22000	254	> 250
B	Boscan 100%	100% SR	1.024	183	40.5	29700	256	> 250
C	Murban 50% Arab light 25% Oman 25%	59% SR 41% B	1.012	197	40.6	13000	177	328
D	Arab light 73% Murban 20% Dubai 7%	64% SR 36% B	1.018	199	38.2	14900	192	344
E	Arab light 4% Murban 87% Oman 9%	58% SR 42% B	1.014	204	38.1	12100	184	338

<sup>a</sup> Measured according to ASTM standard methods.

<sup>b</sup> Composition by mass; SR, straight run vacuum distilled; B, butane precipitated residue.

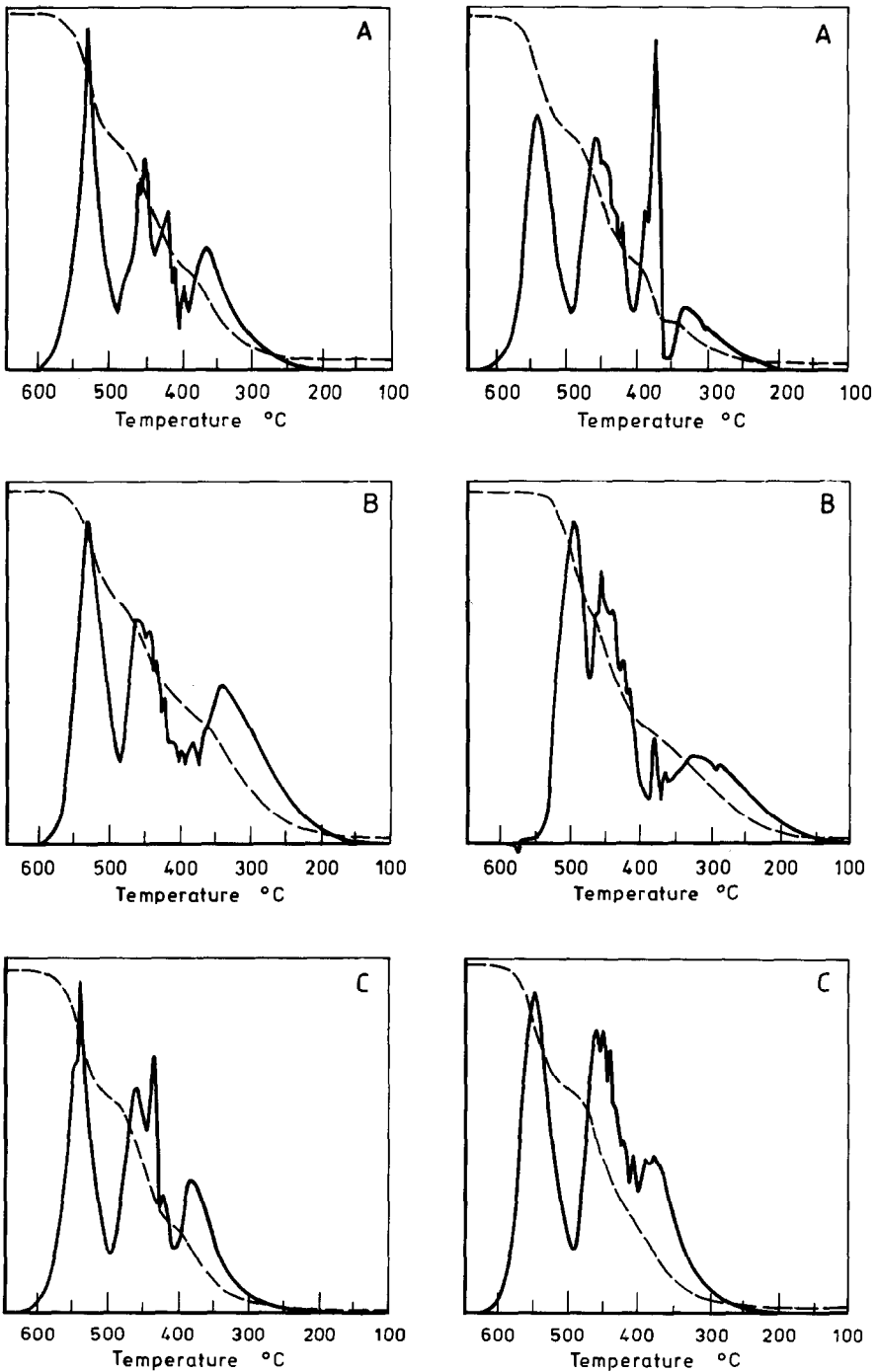


Fig. 1. TG and DTG curves of bitumens A-E in air (heating rate  $15^{\circ}\text{C min}^{-1}$ ): TG, ---, DTG, —.

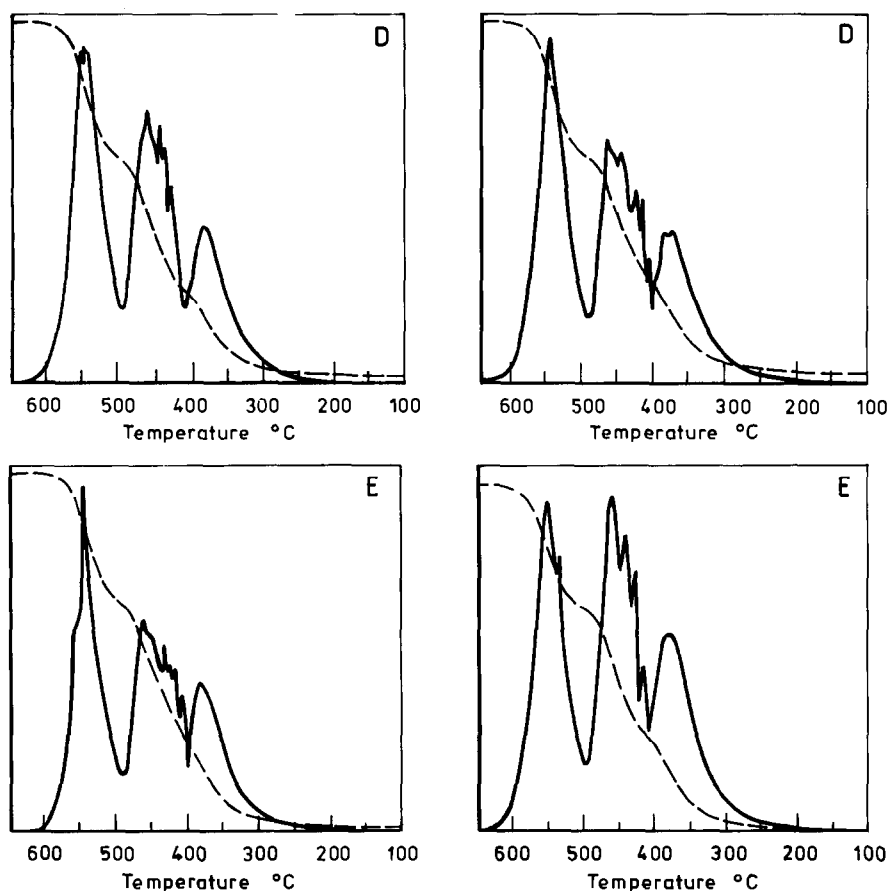


Fig. 1. (continued).

film oven treatment (ASTM D2872) at 163°C, followed by long-term aging in an air stream at 100°C. The time required for a bitumen to reach a “critical” viscosity of  $4.6 \times 10^5$  Pa s at 45°C and a shear rate of  $0.005 \text{ s}^{-1}$  is recorded as the durability value. The bitumens used in the present study had initial viscosities, under the above conditions, ranging from 38 to 74 Pa s. These differences are negligible compared with the final viscosity achieved, so that to all intents and purposes the initial viscosities may be assumed equivalent. This allows a direct comparison of durability values as a measure of oxidative stability.

## RESULTS AND DISCUSSION

### *Non-isothermal experiments*

Initially it was hoped that a comparative measure of oxidative stability for the bitumens studied could be obtained from a rapid non-isothermal

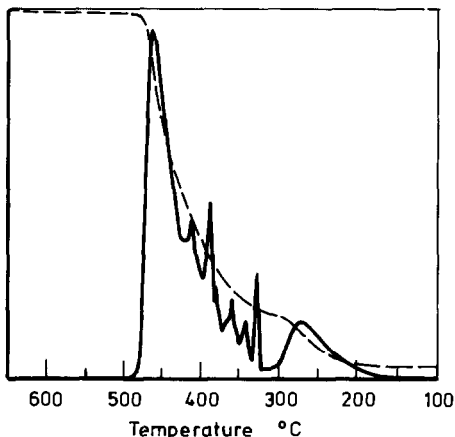


Fig. 2. TG and DTG curves of bitumen A in air (heating rate  $1^{\circ}\text{C min}^{-1}$ ): TG, ---; DTG, —.

experiment. However, the curves obtained, even at low heating rates, were found not to be reproducible enough for this purpose.

Replicate TG and DTG (first derivative) curves in air for each of the bitumens are presented in Fig. 1. The general shapes of the curves are similar to those reported by other workers for petroleum bitumens [7–9] and heavy fuel oils [10] at rapid heating rates. Under air, three steps are observed: at about  $150\text{--}380^{\circ}\text{C}$ ,  $380\text{--}480^{\circ}\text{C}$  and  $480\text{--}600^{\circ}\text{C}$ . Bitumen B is somewhat different in that weight loss begins at a noticeably lower temperature than for the other samples. Interpretation of the curves in terms of the underlying physical and reaction processes occurring is difficult as the profile observed is dependent on heating rate. For example, Fig. 2 shows the TG and DTG curves of bitumen A in air at  $1^{\circ}\text{C min}^{-1}$ . Under these conditions only two steps are observed in the decomposition.

A feature of the DTG profiles is the presence of sharp non-reproducible peaks which can occur at any point in the profile, although they usually appear above about  $380^{\circ}\text{C}$ . These make comparisons of curves from different bitumens in terms of DTG maxima or weight loss data difficult and uncertain, especially given the basic similarity of the curves. Barbooti et al. [9] have reported similar observations during work on Iraqi bitumens. In that study the effect was attributed to the difficult escape of volatile decomposition products, resulting in bubbles which subsequently burst. This explanation seems unlikely in the present case as the peaks are too broad; frothing samples usually produce much sharper peaks, similar to electronic noise. The origin of this non-reproducibility is more likely to lie in the well-documented exothermic nature of bitumen oxidation at elevated temperatures [12]. The heat produced from such reactions may result in the random appearance of “hot spots” within the sample, producing a locally

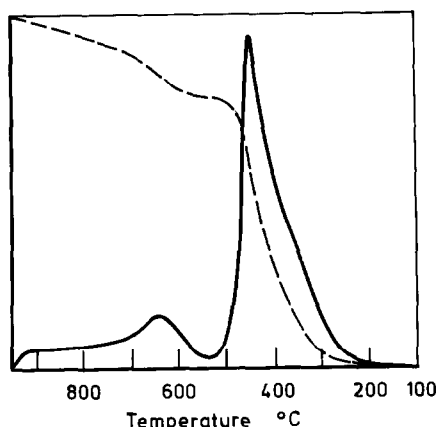


Fig. 3. TG and DTG curves of bitumen A in nitrogen (heating rate  $15^{\circ}\text{C min}^{-1}$ ): TG, ---; DTG, —.

accelerated reaction rate and, hence, rate of weight loss. The hot spot would be quenched as the supply of oxygen available in its vicinity became exhausted and would not be replenished quickly enough through diffusion.

This conjecture is supported by the appearance of the DTG curve for bitumen A in nitrogen (Fig. 3). The random spikes are absent and the curves are reproducible; the same is also true for the other bitumens under the same conditions.

It has been suggested that the TG and DTG profiles obtained in an oxidising atmosphere can be used to fingerprint bitumens from different crudes or manufacturing processes [8]. However, a statistical analysis (ANOVA) of TG weight loss data from the bitumens in the present study [11] showed that at least in this case the TG profiles are not sufficiently reproducible to allow unambiguous fingerprinting.

### *Isothermal experiments*

Methods used for the derivation of kinetic parameters from thermal analysis data have recently been reviewed [13]. The general approach assumes a rate equation of the form

$$d\alpha/dt = k(T)f(\alpha)$$

where  $k$  is the (temperature dependent) rate constant and  $f$  is a function describing the degree of conversion  $\alpha$  ( $\alpha$  is the fractional weight loss in the present case). The temperature dependence of the rate constant is usually assumed to obey the Arrhenius equation

$$k(T) = A \exp(-E_a/RT)$$

Combining these two equations gives

$$d\alpha/dt = A \exp(-E_a/RT)f(\alpha)$$

To avoid the difficulties involved in determining  $f(\alpha)$ , the isoconversional approach described by Friedman [14], and later by Ozawa [15] and Flynn and Wall [16,17], was adopted.

The values of  $(d\alpha/dt)_i$  were determined at fixed degrees of conversion  $\alpha_i$  from a series of isothermal experiments at different temperatures ( $T_i$ ). Plots of  $\ln(d\alpha/dt)$  vs.  $1/T$  were constructed for each bitumen. The rate equation may be rewritten as

$$\ln(d\alpha/dt)_i = \ln Af(\alpha_i) - (E_a/R)(1/T_i)$$

It is apparent that these plots have a slope of  $(E_a/R)$  from which  $E_a$  can be calculated. Thus a knowledge of the form of  $f(\alpha)$  is not required and oxidative stabilities can be compared on the basis of the apparent activation energies. The term apparent is used to emphasise the fact that the measured values are not of fundamental significance. This is because the observed degradation of a complex material such as bitumen is a combination of many different and competing processes. The measured activation energies are thus characteristic of the material as a whole, but are not attributable to any particular molecular process.

The isothermal weight loss curves for bitumen A in air (Fig. 4) are typical of those for all the bitumens studied. As the data were to be

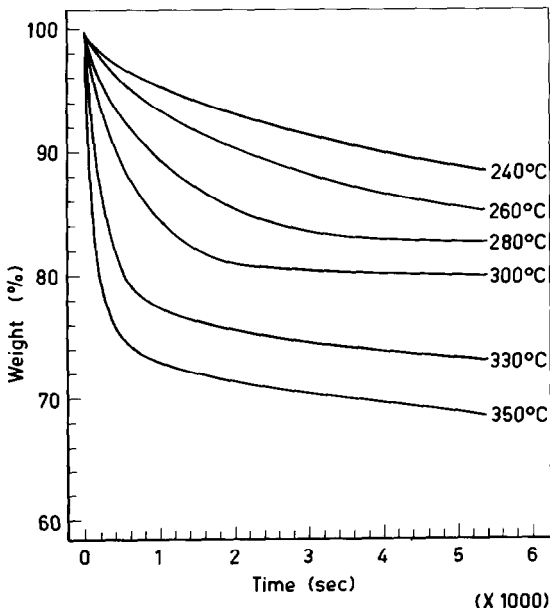


Fig. 4. Isothermal weight loss curves for bitumen A in air at various temperatures.



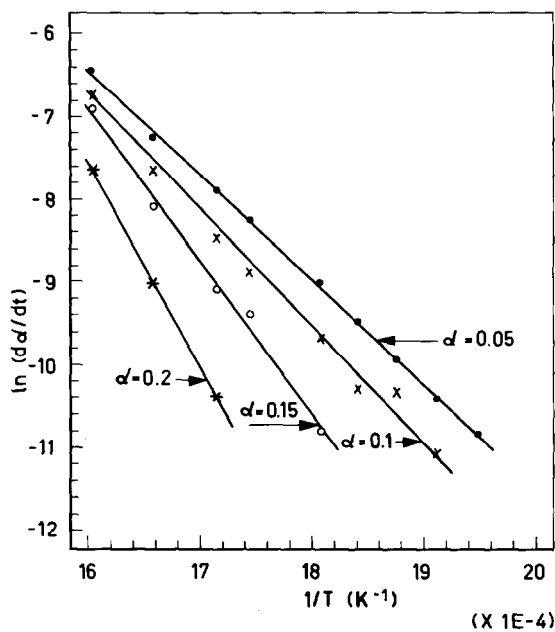


Fig. 5. Arrhenius plots of isoconversional data for bitumen A at various values of  $\alpha$ .

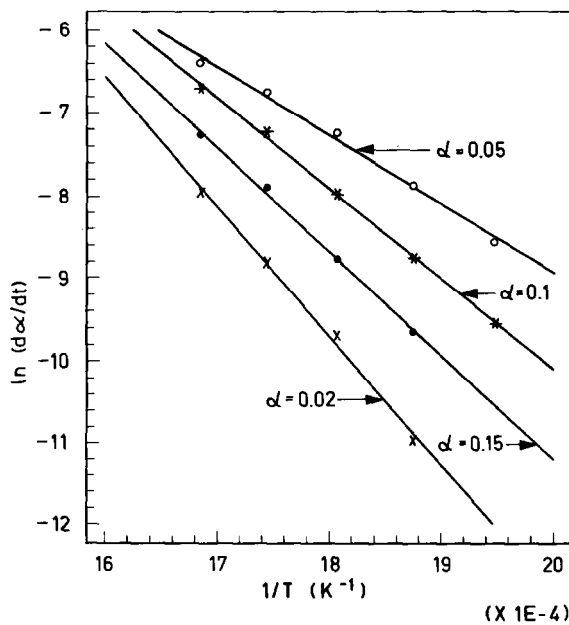


Fig. 6. Arrhenius plots of isoconversional data for bitumen B at various values of  $\alpha$ .

TABLE 2

Apparent activation energies  $E_a$  (kJ mol<sup>-1</sup>)<sup>a</sup>

Bitumen	$\alpha = 0.05$	$\alpha = 0.1$	$\alpha = 0.15$	$\alpha = 0.2$
A	106 ± 3	118 ± 16	155 ± 25	207 ± 30
B	69 ± 9	91 ± 7	104 ± 15	131 ± 28
C	136 ± 19	160 ± 7	—	—
D	129 ± 6	154 ± 15	—	—
E	140 ± 18	169 ± 24	—	—

<sup>a</sup> The errors quoted are based on the 95% confidence limits for the slope of the linear least-squares fit to the relevant isoconversional plots.

compared with oven aging results obtained at 100°C, the isothermal experiments were carried out at temperatures as close to this as possible, with the proviso that weight loss had to be measurable within a reasonable time, given the limitations of the apparatus. In effect, this meant temperatures of 240–370°C and fractional conversions of up to  $\alpha = 0.2$ .

Typical plots of  $(d\alpha/dt)_i$  against  $1/T_i$  (for bitumens A and B) are presented in Figs. 5 and 6, and the calculated values of  $E_a$  in Table 2. The apparent activation energy increases with increasing degree of conversion. This observation is not unexpected in such a complex system, and suggests that the relative importance of various competing processes, with different individual activation energies, changes as the degradation proceeds. A similar increase in  $E_a$  with increasing  $\alpha$  was observed for the degradation of various petroleum and coal tar pitches [18] which, like bitumen, are mixtures of functionalised aromatic and aliphatic hydrocarbons and heterocyclic compounds.

Of particular interest is the lack of dependence of  $E_a$  on temperature, at least over the range studied. To determine whether the relative oxidative stabilities determined from high temperature TG data were maintained during oxidation at lower temperatures (100°C), the  $E_a$  values for  $\alpha = 0.05$  and  $\alpha = 0.1$  were plotted against the durability values for each bitumen (Figs. 7 and 8). The  $\alpha = 0.05$  data show a high degree of correlation ( $r^2 = 99.7\%$ ) for a linear fit; however, the  $\alpha = 0.1$  data show more scatter. This is consistent with the intuitive concept that low TG fractional conversions are more relevant when discussing low temperature aging.

The relationship of low  $\alpha$  to field aging is also clear when considering the processes occurring at low temperatures during the oxidation of petroleum and natural bitumens. The dominant process at temperatures below 200°C appears to be the incorporation of oxygen as ketone, sulphoxide and carboxylic acid functionalities [19–22], probably via hydroperoxide intermediates. This explains the observed proportionate increase in the more polar fractions of the bitumen, in particular the asphaltenes, with aging [23]. Also important are oxidative polymerisation reactions, which

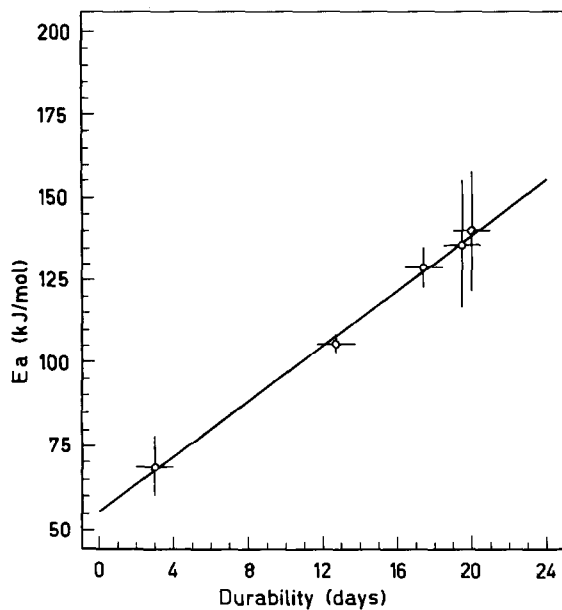


Fig. 7. Correlation between apparent activation energies for  $\alpha = 0.05$  and durability value.

result in higher molecular weight species [24], and dehydrogenation, resulting in increased aromaticity [25]. These processes are thought to be more important at low temperatures [26] than oxidative degradation of larger

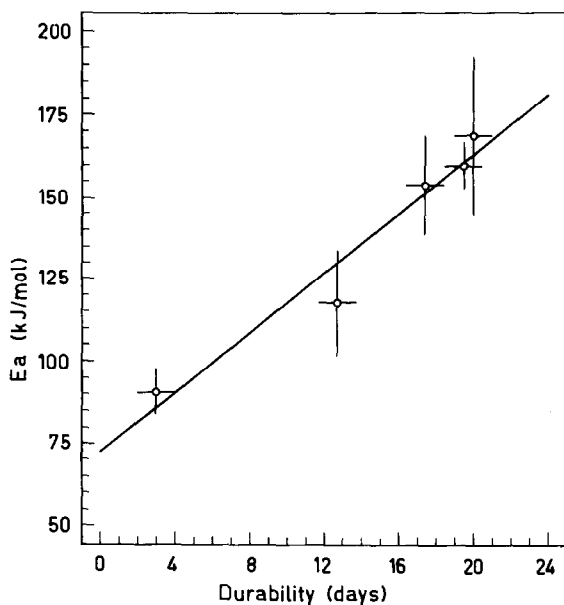


Fig. 8. Correlation between apparent activation energies for  $\alpha = 0.1$  and durability value.

molecules to produce volatile fragments, which would be observed as increasing fractional conversions in a thermogravimetric experiment. Thus the oxidative processes found (and thus the  $E_a$  measured) at large  $\alpha$  are probably less representative of those occurring under milder conditions in the field.

Similarly, simple distillation of the more volatile components of the bitumen is generally considered [27] to be a minor factor in the rate of age hardening. It is therefore reasonable to assume that only a small proportion of the bitumen is being lost in this way, even after many years in the field. Use of low  $\alpha$  values thus allows a relatively more significant contribution to the calculated value of  $E_a$  from this most volatile fraction, which may have been lost at higher  $\alpha$ .

Given the relationship of the durability value to field aging, the good correlation established with  $E_a$  at  $\alpha = 0.05$  suggests that the high temperature TG measurements may thus be useful in predicting the low temperature oxidative behaviour of roading bitumens.

## CONCLUSIONS

Apparent activation energies derived from isothermal TG data for several petroleum bitumens were found (over the range studied) to be independent of temperature, but (consistent with their complex composition) dependent on the fractional conversion. The values of  $E_a$  obtained at low fractional conversion were found to correlate well with durability oven data. These data have in turn been correlated with field aging of bitumens. Although in the present study the correlation is based on only a limited number of materials, these comprised bitumens with very different crude sources and manufacturing histories. When developed further, this relationship will allow, at the very least, an easier and more rapid determination of durability values. It also seems that further work to relate TG kinetic data directly to field aging is well warranted.

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## REFERENCES

- 1 F.L. Roberts, P.S. Kanahal, E.R. Brown, D.Y. Lee and T.W. Kennedy, Hot Mix Asphalt Materials Mixture Design and Construction, NAPA Education Foundation, Lanham, MD, 1991.
- 2 J.C. Petersen, Proc. Assoc. Asphalt Paving Technologists, 58 (1989) 220.

- 3 O.K. Kim, C.A. Bell, J.E. Wilson and G. Boyle, *Transp. Res. Rec.*, (1115) (1989) 101.
- 4 Australian Standard 2341, *Methods of Testing Bitumen and Related Products*, Standards Association of Australia, 1980.
- 5 E.J. Dickinson, *Proc. 11th Australian Road Research Board Conf.*, 11 (3) (1989) 35.
- 6 J.W.H. Oliver, *Transp. Res. Rec.*, (1106) (1987) 116.
- 7 J. Donbavand, G.F.A. Ball and J.E. Patrick, *Thermochim. Acta*, 98 (1986) 99.
- 8 F. Al-Sammerrai and D. Al-Sammerrai, *Thermochim. Acta*, 94 (1985) 295.
- 9 M.M. Barbooti, H.H. Al-Soufi, H.E. Al-Saleem and E.B. Hassan, *J. Pet. Res.*, 6 (1987) 145.
- 10 I.W. Cumming, *J. Inst. Energy*, (1981) 201.
- 11 P.R. Herrington, unpublished data, 1991.
- 12 E.J. Barth, *Asphalt Science and Technology*, Gordon and Breach, London, 1962, Chapter 6.
- 13 K.N. Nihan, *J. Therm. Anal.*, 35 (1989) 1267.
- 14 J.L. Friedman, *J. Polym. Sci.*, 50 (1965) 183.
- 15 T. Ozawa, *Bull. Chem. Soc. Jpn.* (1965) 1881.
- 16 J.H. Flynn and L.A. Wall, *Polym. Lett.*, 4 (1966) 323.
- 17 J.H. Flynn, *J. Therm. Anal.*, 27 (1983) 95.
- 18 G.W. Collett and B. Rand, *Thermochim. Acta*, 41 (1980) 153.
- 19 J.C. Petersen, F.A. Barbour and S.M. Dorrence, *Anal. Chem.*, 47 (1975) 112.
- 20 S.M. Dorrence, F.A. Barbour and J.C. Petersen, *Anal. Chem.*, 46 (1974) 2242.
- 21 J.C. Petersen, *Prepr., Div. Pet. Chem., Am. Chem. Soc.*, 26 (1981) 898.
- 22 J.C. Petersen and H. Plancher, *Anal. Chem.*, 53 (1981) 786.
- 23 D.R. Babu and D.E. Cormack, *Fuel*, 63 (1984) 858.
- 24 A.S. Noureldin and L.E. Wood, *Transp. Res. Rec.*, (1228) (1990) 191.
- 25 S.E. Moschopedis and J.G. Speight, *Fuel*, 54 (1975) 210.
- 26 S.E. Moschopedis and J.G. Speight, *Fuel*, 52 (1973) 83.
- 27 L.W. Corbett and R.E. Merz, *Transp. Res. Rec.*, (544) (1975) 27.