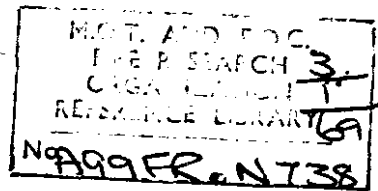# Fire Research Note
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THE DARKENING OF IRRADIATED WOOD SURFACES

by

S. J. MELINEK

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SUMMARY

The degree of darkening of wood surfaces has been used to estimate the amount of heat received by a surface in circumstances where many rough measurements obtained with little effort are preferable to a few highly accurate measurements. Griffiths and Heselden[1] have calibrated blocks of wood for this purpose. It is of interest to explore the use of the rate of darkening as a measure of the incident heat flux. Accordingly, the results obtained by Griffiths and Heselden have been re-examined. It is shown that the darkening follows a first order law and time constants are obtained for several incident flux densities. An activation energy is obtained from the variation of the time constant with the surface temperature of the wood and an equation is derived giving the intensity of irradiation as a function of the degree of darkening and the time of exposure.

· It is shown that the rate of darkening, as measured by the reflectivity of light from a tungsten filament lamp, has rate constants very similar to that governing the rate of pyrolysis.

KEY WORDS: Radiation, Measurement, Pyrolysis, Wood, Rate, Arrhenius Equation.

MINISTRY OF TECHNOLOGY AND FIRE OFFICES' COMMITTEE

JOINT FIRE RESEARCH ORGANIZATION

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1. INTRODUCTION

The darkening of wood surfaces has been used to estimate radiation flux densities by Griffiths and Heselden[1], who measured the reflectivity of the surfaces for light from a tungsten filament lamp. Here the results are analysed to study the rate of darkening.

2. ESTIMATION OF SURFACE TEMPERATURE

The rate of darkening varies with the surface temperature, which depends on the rate of heating. Values obtained by Griffiths and Heselden for the surface temperatures at different heating rates are given in the following table. These values were obtained by the use of temperature sensitive papers.

Table 1

Surface Temperatures

Incident radiation flux density, I, W cm^{-2}	0.22	0.32	0.43
Surface temperature after 30 mins, T_{30}, °K	383 ·	411	444

For the purposes of this paper it is necessary to estimate temperatures at somewhat higher intensities and these were obtained by assuming an effective cooling constant, h.

h = convective cooling constant, h_c

+ radiative cooling constant, h_r

Taking h_c = 0.0013 W cm^{-2} degC^{-1} as a mean value for the temperature range

and h_r = 4 $\varepsilon \sigma T^3$ from the Stefan Boltzmann law,

gives h = 0.0042 W cm^{-2} degC^{-1}

T is an average temperature, taken as 520°K

and ε is the emissivity, taken as 0.9.

2. ESTIMATION OF SURFACE TEMPERATURE (cont'd)

Simms and Law[2] have pointed out that the emissivity of many surfaces is higher in the case of thermal radiation from a low temperature source than for shorter wave lengths from a higher temperature source. The value assumed is that used by Koohyar[3].

The variation of the surface temperature with time, where the rate of cooling varies linearly with the surface temperature, can be calculated (see Carslaw and Jaeger[4]). For these experiments and this wood, calculations show that the equilibrium surface temperature, T_∞, is about 15 per cent higher than T_{30}.

The variation of T_∞ is given by

$$h\,T_\infty = I$$

i.e. $\quad h\,T_{30} \doteq 0.85\,I$

3. RATE OF REACTION

If we assume that the reflectivity of the surface decreases due to a first order chemical reaction, then, when the surface temperature has reached an approximately steady value,

$$(d/dt)\,(r-r_\infty) = -K(r-r_\infty)$$

giving $r-r_\infty = A\exp(-Kt)$ for an isothermal change

$$\ln\left(r/r_0 - r_\infty/r_0\right) = B - Kt$$

where A, B are constants;

r_0, r, r_∞ are the reflectivities (for light from a tungsten filament lamp) initially, after time T, and after long times, respectively;

K is a rate constant.

The results showed that r_∞/r_0 was approximately 0.1 and this value was used in the calculations. Fig. (1) shows that, for several values of I, $\log(r/r_0 - r_\infty/r_0)$ varied linearly with t. Thus the darkening of the surfaces can be represented by a first order chemical reaction. It is necessary, for this approximate treatment, to assume a mean effective constant value of T and for convenience the value after 30 mins heating may be taken for this.

3. RATE OF REACTION (cont'd)

Values of the rate constant, K, for different intensities are given below together with the surface temperatures estimated from the experimental results and equation (1)

Table 2

Rate Constants

I, W cm^{-2}	0.42	0.62	0.84	1.05	1.26
K, min^{-1}	0.007	0.039	0.097	0.143	0.543
T_{30}, ^{o}K	441	480	519	558	597

Log K versus $10^3/T_{30}$ is plotted in Fig. (2), which shows that log K varies linearly with $1/T$. Thus the rate constant is consistent with an equation of the Arrhenius form. The reaction has an activation energy, E, of 57 kJ/mole and a frequency factor of 4.1×10^4 min^{-1}.

Within this range of intensity of irradiation the effective constant value can be obtained from the formulae

$$K = 4.1 \times 10^4 \exp(-E/RT) \text{ min}^{-1} \qquad (3)$$

$$= 4.1 \times 10^4 \exp(-1/(0.532 + 0.274I)) \text{ min}^{-1} \qquad (4)$$

where I is the intensity in W cm^{-2}.

$$Kt = \ln \frac{r_o - r_\infty}{r - r_\infty} \qquad (5)$$

From equations (4) and (5)

$$I = 3.65 \left(\ln(4.1 \times 10^4 t) - \ln \ln \frac{r_o - r_\infty}{r - r_\infty} \right)^{-1} - 1.94 \text{ W cm}^{-2}$$

It is possible to allow for the effect of the variation in surface temperature but this would introduce complications in the analysis which are probably unwarranted for the immediate purposes of this paper. However, if the intensity were also varying in time a more detailed analysis would be

necessary. Nevertheless equation (3) (though not equation (4)) is of the form which is appropriate to a time varying situation and accordingly could be used, in conjunction with a transient relation between surface temperature and heating rate to give a first approximation to a calibration for, say, a time varying intensity.

4. FURTHER OBSERVATIONS ON PYROLYSIS

The variation of the rate constant for the main pyrolysis reaction, calculated from values given by Roberts and Clough, is shown in Fig.(2). It can be seen that the rates of darkening and of pyrolysis are of the same order.

The darkening and pyrolysis are both due to thermal degradation. Since the darkening and pyrolysis have similar rate constants the darkening could be used as a measure of the degree of pyrolysis. It is likely that they are due to the same reactions.

Measurements showed that easily removable char was not formed until the darkening reaction was nearly complete. Moreover, heavily charred wood was a somewhat shiny black while darkened wood had a brown coloration. There was a sharp boundary between the char and the underlying wood. The char could be removed by means of a wire brush, which did not remove any of the wood, showing that the strength of the wood, even just beneath the char, was greater than that of the char. Thus it appears that char formation occurs late in the pyrolysis and may be due to a different process. The sharp boundary suggests that char formation has a high activation energy.

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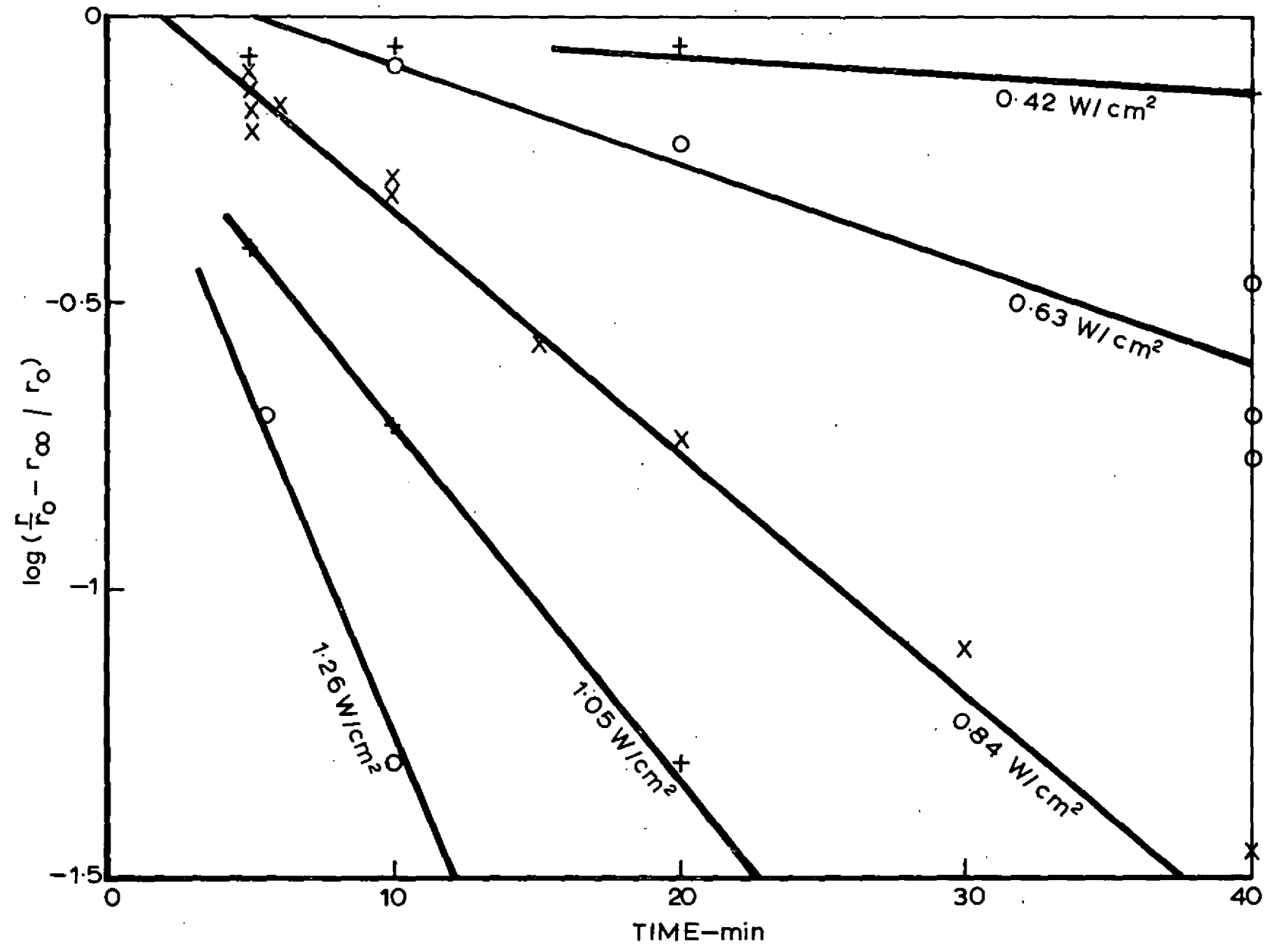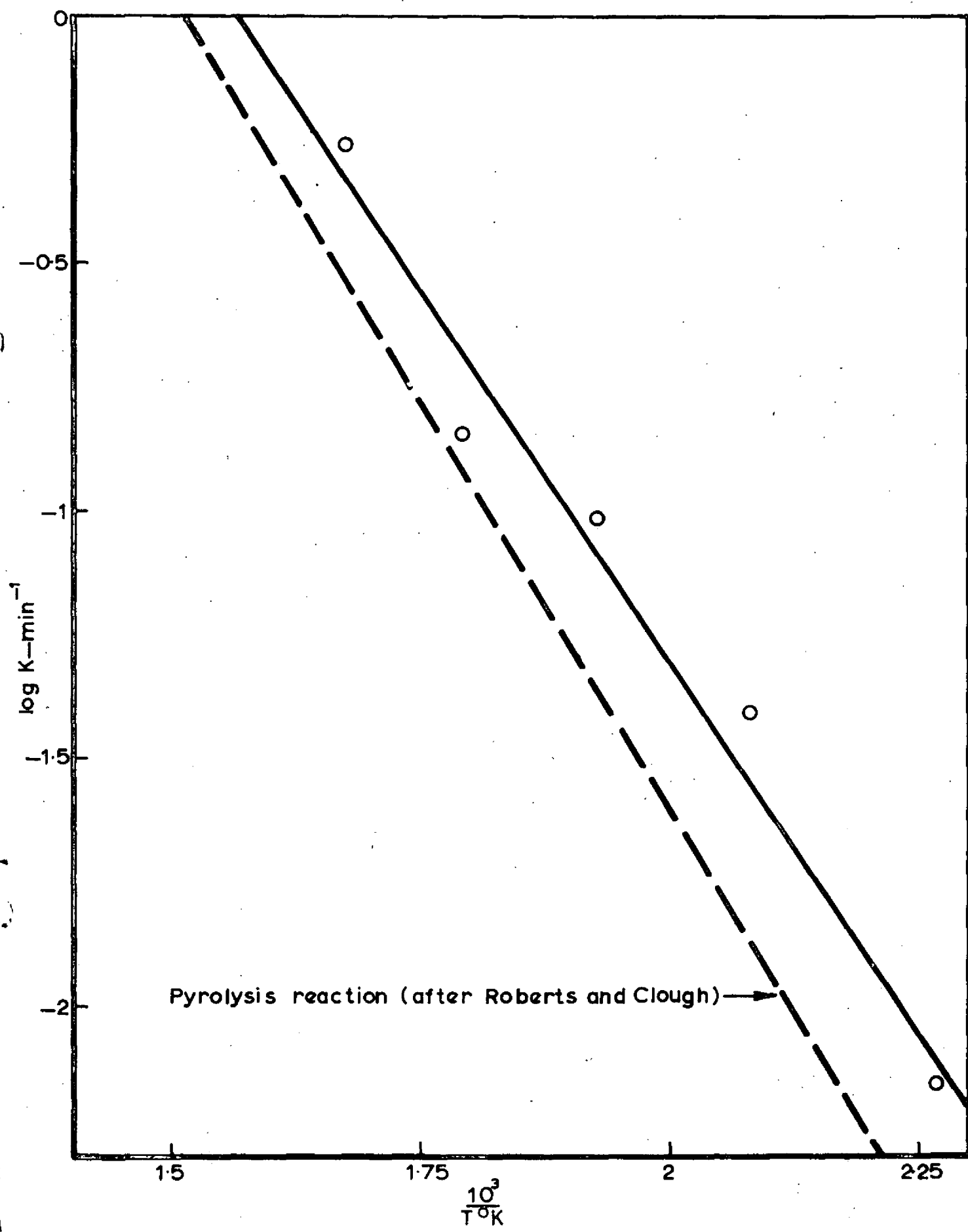5. ROBERTS, A. F. and CLOUGH, G. Ninth Symposium (Int.) on Combustion. Academic Press, 1963. p.158-165.

FIG. 1. VARIATION OF REFLECTIVITY

FIG. 2. VARIATION OF RATE CONSTANT

Pyrolysis reaction (after Roberts and Clough)

log K—min⁻¹

$\frac{10^3}{T^\circ K}$

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