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SELF-HEATING AND IGNITION IN TWO-COMPONENT SYSTEMS
PRELIMINARY EXPERIMENTAL STUDY

by

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SUMMARY

Observations have been made on self-heating and ignition of cubes of sawdust containing a fatty oil (olive oil). Preliminary comparison with a theoretical model for two component systems (unpublished) shows that the relationship between the critical temperature rise and critical ambient temperature for ignition has the general form required by the model.

MINISTRY OF TECHNOLOGY AND FIRE OFFICES' COMMITTEE

JOINT FIRE RESEARCH ORGANIZATION

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INTRODUCTION

Many practical examples of self-heating and ignition involve the oxidation
of a limited quantity of a fatty oil distributed on a porous combustible
substrate. Amonth these examples are fishmeal, certain oilseed cakes and
animal feeding-stuffs, and oiled textile fibres including the well-known
'oily rag'.

Laboratory investigations made in the course of dealing with enquiries on self-
heating in such materials have disclosed behaviour more complex than can be
accounted for directly by some existing theoretical models of self-heating.
These complications have led to difficulties in attempting to predict large-
scale self-heating behaviour from the results of small-scale laboratory tests.

This note presents the results of the determination of minimum ambient
temperatures for the ignition of some oil-sawdust mixtures, containing
differing concentrations of oil, in the shape of cubes of differing sizes.
Mixed hardwood sawdust studied in earlier work on ignition[1,2] was used, and
the oil was olive oil. This oil tends to show borderline self-heating behaviour
in the Mackay test.

The object of this work has been to obtain some basic data against which
a theoretical model for self-heating and ignition in two-component systems
(to be reported elsewhere) can be tested. This work was carried out as a
short-term project and it was not possible in the time available to examine
large sizes of specimens.

EXPERIMENTAL

a) Materials

The mixed hardwood sawdust was a relatively coarse fraction of the batch
used previously. Sieve analyses showed 80 per cent in the range 18-25 B.S.
mesh and 0.3 per cent finer than 60 mesh. The average moisture content was
10.1 per cent.

The olive oil used was B.P. grade; its density was not measured but
taken as 0.92 g cm^{-3} from tables[3]. As a measure of its reactivity the iodine

value of the oil was determined by the standard Wijs' method[4]. The value obtained was 82 ± 1.5 g of iodine per hundred g of oil.

b) Apparatus

The oiled sawdust was packed into cubical wire baskets, made of 40 mesh brass gauze to the appropriate sizes. These baskets were suspended at the centre of an ordinary oven capable of maintaining a given temperature to within ± 1°C over long periods of time. Forced convection was employed within the oven.

Temperatures were measured with the aid of two 36 S.W.G. chromel-alumel thermocouples. One was suspended within the oven at 2-3 cm from the sample; the other was arranged to be as near as possible to the centre of each basket for following the course of the self-heating and ignition. Cold junctions were at 43°C.

Temperatures were recorded in all cases on a multipoint chart recorder but, also, some critical temperatures were measured potentiometrically as a check on the recorder.

c) Procedure

The weights of sawdust were chosen to correspond as nearly as possible with a packing density of 0.20 g cm^{-3} in all experiments. Oil was mixed with the sawdust by hand at room temperature and the amounts used are shown in Table 1.

Table 1

Weights of sawdust and oil

Cube size cm	Weight of sawdust g	Weights of oil g				
2.5	3.33	–	0.226	0.452	0.904	1.808
5.1	26.7	–	1.808	3.616	7.232	–
7.6	90.0	3.035	6.07	12.14	24.28	–
Oil/sawdust ratio w/w		0.034	0.068	0.136	0.27	0.54
Oil content* % w/w		3.29	6.4	12.0	21	35

*Wt of oil x 100/(wt of oil + wt of sawdust)

A freshly oiled mixture was packed into a wire basket and then suspended for test in the oven, which had been preheated to the desired temperature.

d) Ignition temperatures

Experiments were performed at a series of oven temperatures which differed by 5°C. As previously[1,2], a temperature was found at which ignition occurred and which was 5°C higher than the maximum temperature at which no ignition occurred in two or three repeated tests. The ignition temperature was then taken as the mean of the minimum temperature at which ignition was observed and the maximum lower non-ignition temperature. A few experiments were performed at temperature intervals of less than 5°C.

RESULTS

Typical temperature records for self-heating and ignition of the cubes of sawdust with and without oil are shown in Fig.1 for 7.6 cm cubes. The earlier part of the records below 100°C, not shown here, included a plateau in the neighbourhood of 70°C which was attributed to loss of moisture. The following features should be noticed:-

1. At an ambient temperature just too low for ignition, i.e. 190°C, and following the loss of moisture, the temperature at the centre of the cube of unoiled sawdust increased continuously, and without inflecting, to a maximum of 31°C above the oven temperature and then slowly decreased.

2. At a higher ambient temperature, 195°C, the unoiled sawdust ignited and burned to ash. The temperature record at the centre showed an upward inflexion at 32°C above ambient, i.e. in the neighbourhood of the maximum excess temperature when no ignition occurred.

3. The temperature records for the oiled sawdust in both cases showed an upward inflexion at about 5°C above the oven temperature. This is consistent with the autocatalytic character of the oxidation of fatty oils.

4. Following the first inflexion, the temperature at the centre of the oiled sawdust at an ambient temperature of 140°C, rose to a maximum 98°C above ambient and then decreased. At this maximum, the actual value of the centre temperature was 238°C and the sawdust was found to be charred at the end of the test.

5. At an ambient temperature 5°C higher (145°C) the cube of oiled sawdust ignited and burned to ash. The temperature record showed an upward inflexion at 100°C above ambient, i.e. on the neighbourhood of the maximum reached when no ignition occurred.

6. The inflexions in the neighbourhood of 400°C in the temperature records for both oiled and unoiled sawdust are post-ignition effects and outside the range of immediate interest. They are probably explicable in terms of oxygen starvation as the rate of consumption became very high, followed by improved oxygen supply as the charred cube began to shrink and crack open.

Table 2

Self-heating and ignition results for
sawdust/oil mixtures

Cube size cm	Oil content %	Ignition temperature °C	ΔT_{max} sub-critical °C	ΔT_{min} inflexion °C	ΔT critical °C
2.54	0	232	20	20	20
	6.4	228	29	53	42
	12.4	222	60	62	61
	21.0	203	94	107	101
	35	197	110	105	108
5.1	0	203	24	26	25
	6.4	194	54	58	56
	12.4	168	94	100	97
	21.0	148	137	125	130
7.6	0	188	31	32	32
	3.3	183	28	40	34
	6.4	168	58	75	67
	12.4	143	98	100	99

The results of all tests are summarized in Table 2 which gives the critical ambient temperature for each cube size and oil content, the maximum sub-critical temperature rise (ΔT_{max}) observed when no ignition occurred and also the minumum temperature rise (ΔT_{min}) at the upward inflexion when ignition did occur; the mean of these last two values is listed as an estimate of the critical temperature rise for ignition (ΔT). The last two quantities were often reproducible to within a few degrees at a given ambient temperature and were normally close together; the occasional large discrepancies in the table are probably due to

occasional lack of uniformity in the mixing of the oil and sawdust.

The reduction in ignition temperature for each size of cube as the oil content was increased is shown in Fig.2, and the dependence of the critical temperature rise, ΔT, on the oil content is shown in Fig.3.

DISCUSSION

General

As noted previously[1,2,5] the ignition behaviour of untreated sawdust, and other cellulosic materials can be satisfactorily described in terms of a thermal ignition model which assumes a single reactive component obeying approximately zero order kinetics; although for wood fibre insulating board, the detailed comparison of self-heating data and ignition data indicated the presence of a second, short-lived, reaction[5].

The critical temperature rise in the untreated sawdust is of the expected magnitude, i.e. about 25 deg.C, but it also shows a small increase as the specimen size becomes larger and ignition temperature becomes lower. This effect has not been previously commented upon and does not appear large enough seriously to invalidate the use of a single component ignition model but, in the light of the present work, it provides some evidence of a subsidiary reaction contributing to the ignition.

Ignition temperatures for the untreated sawdust are about $5^{\circ}C$ higher than for the finer fractions used previously[1,2], and the apparent activation energy, determined from a plot of the ignition data[5], is about 25,000 cal/mole compared with about 23,000 cal/mole for the finer fraction.

The oiled sawdust shows relatively sharply defined ignition behaviour in the same way as the untreated sawdust. However, the critical temperature rise increases with oil content up to several times the value which would be expected for ignition in a one-component system. This is a feature that has been often observed in self-heating tests on other materials containing fatty oils. At at given oil content, the effect of the oil on ignition temperature and on the critical temperature rise (Figs 2 and 3) becomes more pronounced as the specimen size is increased and the ignition temperature becomes lower.

Comparison with theoretical model

A theoretical model appropriate to systems of two reactive components such as the oiled sawdust, and comparison with the above results, is to be reported in detail elsewhere. It is possible here, however, to outline briefly the relation between the critical temperature rise and the ignition temperature for the oiled sawdust.

The simplest two-component model assumes a mixture consisting of an exhaustible component (component 2) obeying simple kinetics of order greater than zero and an effectively inexhaustible component (component 1) obeying zero order kinetics. First, it may be noted that the steady states for the system when only component 1 is reactive and component 2 is present as an inert diluent, and when certain widely used approximations are made in the equation for the heat balance, are represented by

$$\delta_1 / \delta_c = \theta \, e^{(1-\theta)} \tag{1}$$

where

$$\delta_1 = \frac{E_1}{RT_o^2} \, r^2 \, \frac{m_1}{m_1 + m_2} \, Pe^{(-E_1/RT_o)},$$

$$\theta = \frac{E_1}{RT_o^2} \, (T - T_o) \, ,$$

E_1 = activation energy for reaction of component 1;

R = gas constant; T, T_o = centre and ambient temperatures (^{o}K) respectively;

r = half side of cube; P = constant depending on physical and chemical properties of the systems;

and m_1 and m_2 are the masses of component 1 and component 2 respectively present in the system.

δ_1 is the Frank-Kamenetskii self-heating parameter for the system when component 2 is inert and $_1\delta_c$ is its critical value, which, for the cube is 2.53[5]. θ is the temperature rise in dimensionless form. For any value of δ_1 / δ_c less than unity, equation (1) has two solutions for θ; solutions for which $\theta < 1$ represent stable steady states, and those for which $\theta > 1$ represent unstable steady states.

The ratio $\mathcal{S}_1/_1\mathcal{S}_c$ defines a temperature scale in terms of the ignition temperature for a given size and shape of the two component mixture when component 2 is inert. It can be shown that the critical condition for ignition, when component 2 is reactive, can be expressed in terms of a critical value of the ratio $\mathcal{S}_1/_1\mathcal{S}_c$ at which the temperature rise, Θ, is given by the corresponding upper solution of equation (1) just as component 2 becomes exhausted.

For purposes of relating the observed critical ambient temperatures and temperature rises for the oiled sawdust, the quantities $\mathcal{S}_1/_1\mathcal{S}_c$ and Θ are calculated as follows:-

$$\frac{\mathcal{S}_1}{_1\mathcal{S}_c} = \left(\frac{T_o^1}{T_o}\right)^2 \; \mathcal{e}^{-\frac{E_1}{R}\left(\frac{1}{T_o} - \frac{1}{T_o^1}\right)} \tag{2}$$

$$\Theta = \left(\frac{T_o^1}{T_o}\right)^2 \cdot \frac{\Delta T \text{ (oiled)}}{\Delta T \text{ (unoiled)}} \tag{3}$$

where T_o is the ignition temperature of a cube of given size and oil content and T_o^1 is the ignition temperature for a cube of unoiled sawdust of the same size which has been corrected for the hypothetical presence of component 2 as an inert diluent. It can be shown that, provided the oil content is not large, this corrected value is given by

$$T_o^1 = T_o + \frac{m_2}{m_1 + m_2} \cdot \frac{RT_o^2}{E_1}$$

where, here, T_o is the ignition temperature for the unoiled sawdust. The correction is negligible when the oil content is small, and amounts to only $7^\circ C$ for the 2.54 cm cube containing 35 per cent oil.

The experimental results, converted as above, are plotted in Fig.4, together with the curve given by equation (1). It will be seen that the results lie about the upper branch of equation (1) as the model requires. The differences from the expected relationship (continuous curve) shown by the results for the 2.54 cm and 7.6 cm cubes follow the observed trend in the critical temperature rise for the unoiled sawdust, the quotients in equation (3) being higher than expected for the small size and smaller for the large size. If the effect of

this trend is eliminated by using a mean value for the critical temperature rise for the unoiled sawdust, all values of θ in Fig.4 lie within 10 per cent of the value expected from equation (1).

The relationship between the critical temperature rise and critical ambient temperature, for cubes of oiled sawdust of different sizes and containing different quantities of oil, clearly has the general form expected on the basis of the theoretical model. The deviations arise from a complication in the self-heating reactions of the sawdust itself. It will have been noticed that the relationship takes no account of the reaction kinetics for component 2; this can be shown to be quite general. A knowledge of these kinetics is, however, required for calculating critical values of $S_1/_1S_c$ from first principles, as will be shown elsewhere.

This limited experimental study represents an initial attack on a problem of considerable importance to the correct assessment of the self-heating behaviour of a wide range of commodities. Extensions of the work most immediately required are studies on a larger scale than could be attempted here and, also, on components exhibiting a wider range of kinetic behaviour.

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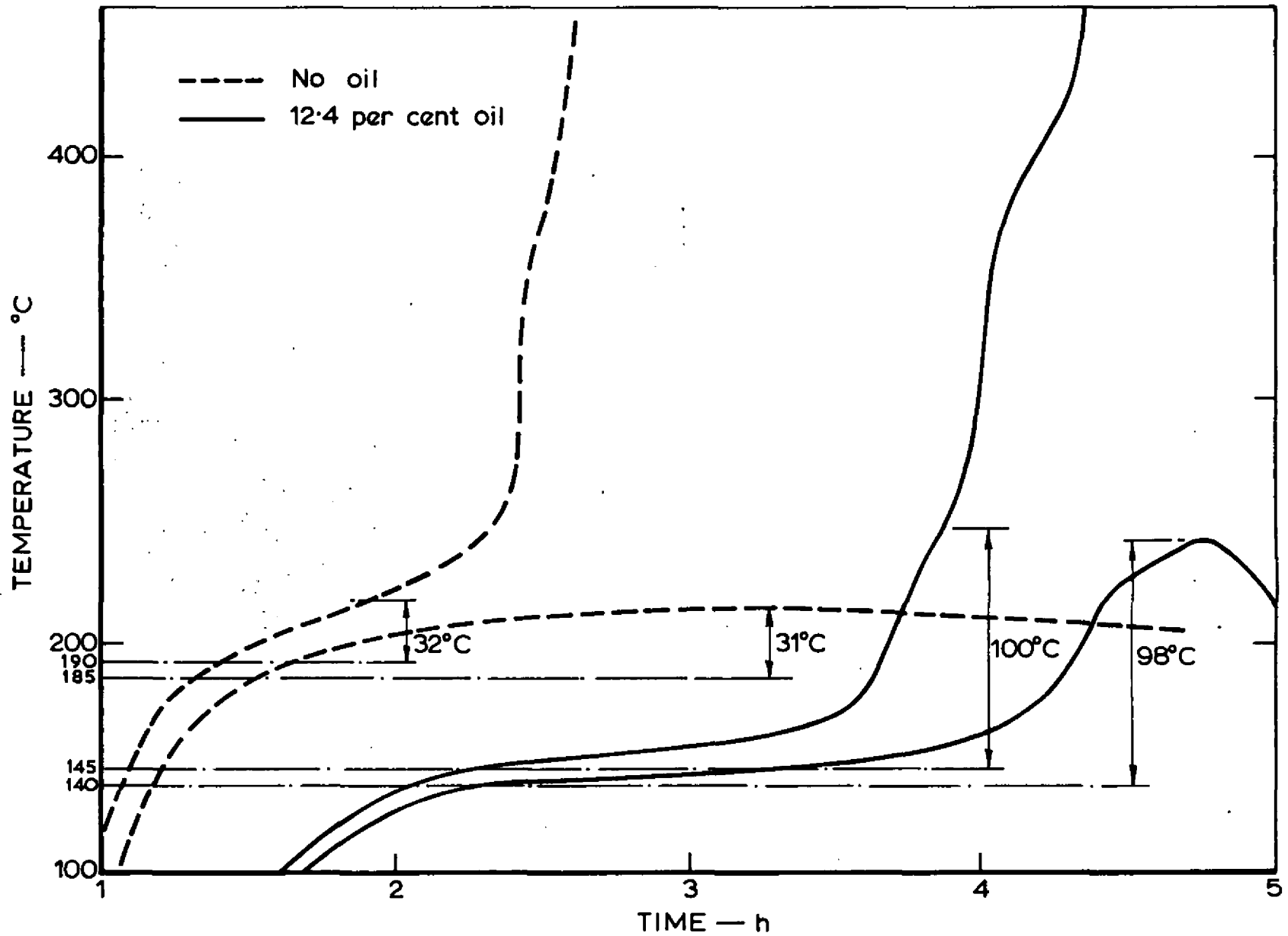
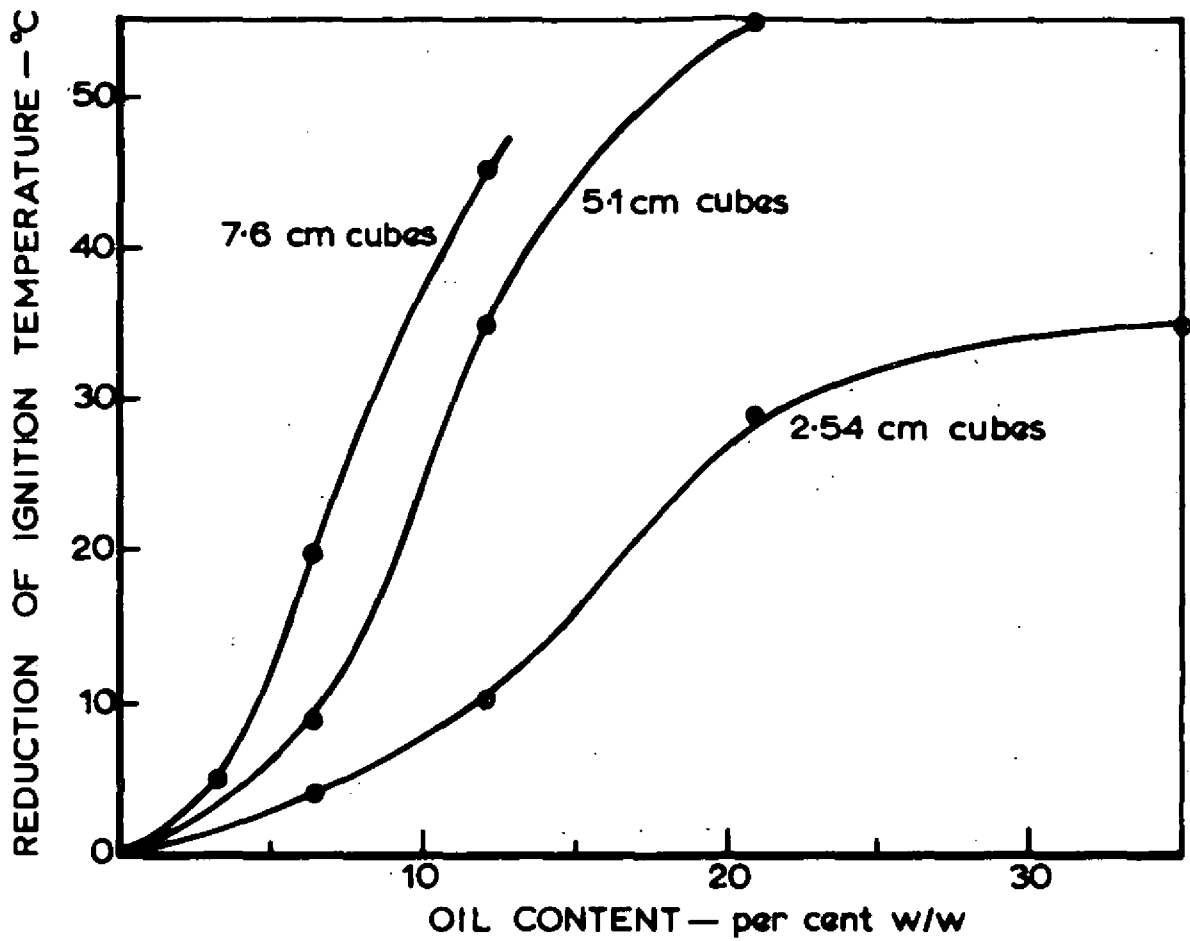FIG. 1.   SELF-HEATING   AND   IGNITION   OF   SAWDUST   CUBES

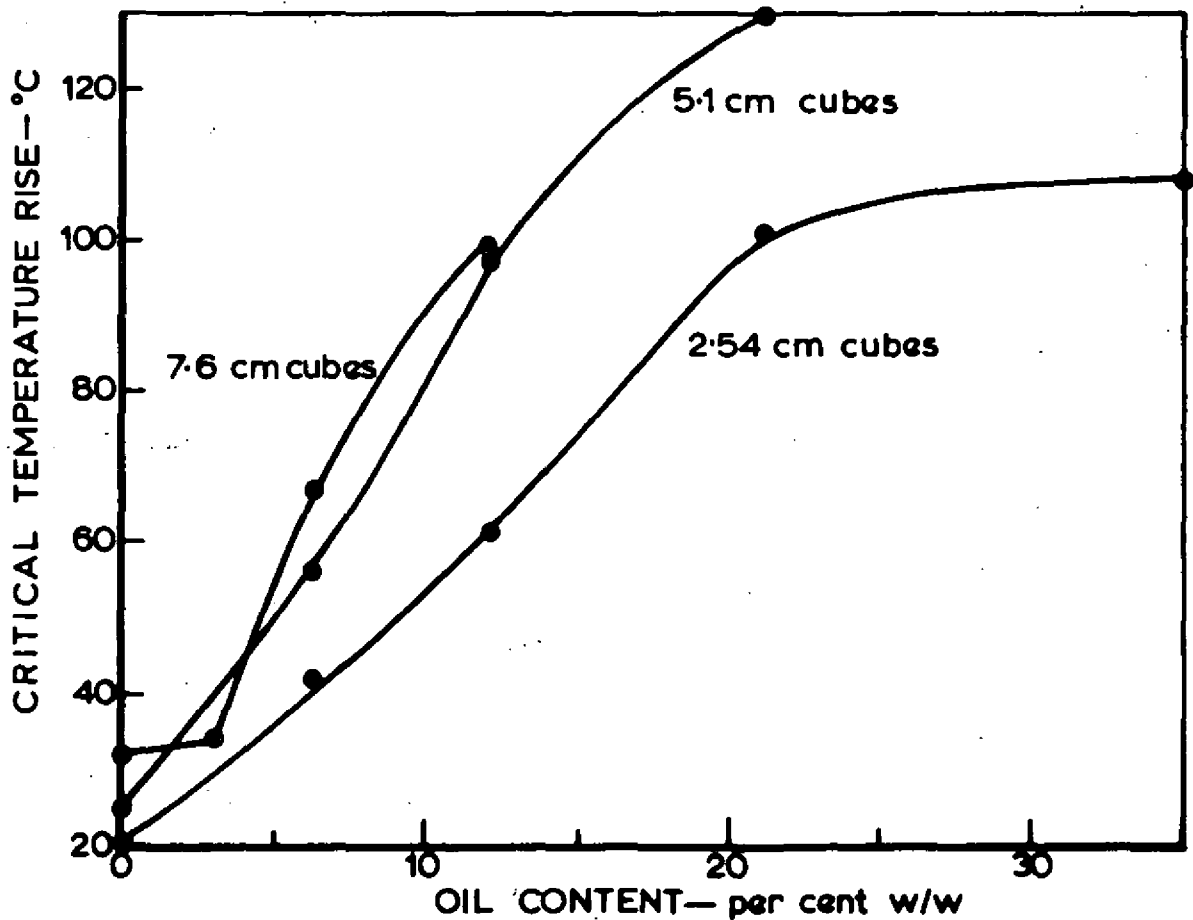FIG. 2. EFFECT OF OIL CONTENT ON IGNITION TEMPERATURE

FIG. 3. EFFECT OF OIL CONTENT ON CRITICAL TEMPERATURE RISE
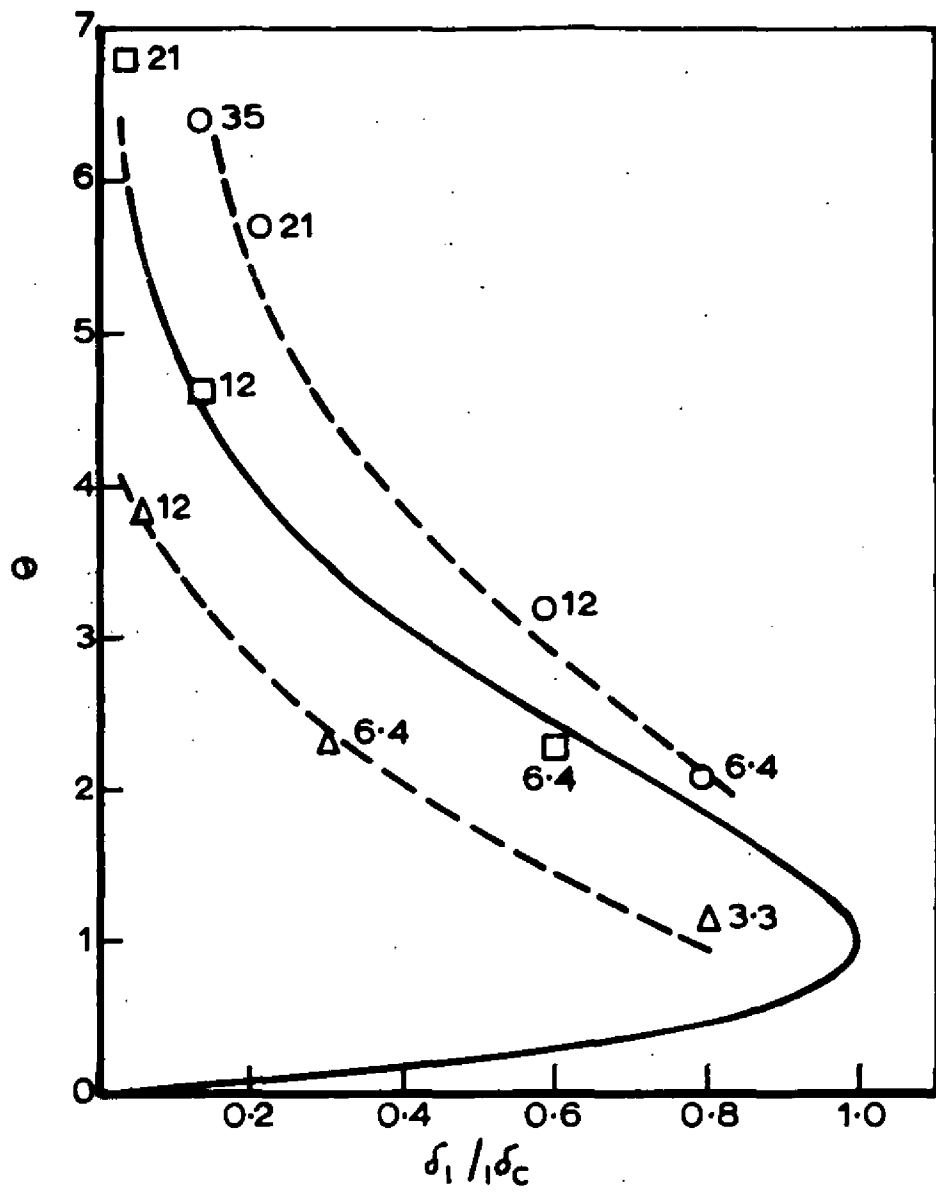
FIG. 4. CRITICAL TEMPERATURE RISE FOR CUBES OF OILED SAWDUST