CRITERIA FOR AUTOIGNITION OF COMBUSTIBLE FLUIDS IN INSULATION MATERIALS

J. Brindley[3], J F. Griffiths[1], N Hafiz[2], A C. McIntosh[2] and J Zhang[1]
School of Chemistry[1], Department of Fuel and Energy[2] and School of Mathematics[3],
The University, Leeds LS2 9JT, UK

Criteria have been investigated for the conditions at which a "lagging fire" may occur when a flammable liquid penetrates and is dispersed within insulation material surrounding a hot pipe. The conditions at which a Frank-Kamenetskii thermal ignition criterion should be replaced by one derived from the heat release rate versus fluid evaporation rate were deduced. These conditions were related to the decreasing enthalpy of vaporisation of the fluid. Practical investigations were based on formal "cube test" methods for thermal ignition. The theory was tested against the behaviour of n-$C_{16}H_{34}$, n-$C_{18}H_{38}$ and n-$C_{20}H_{42}$, which represent alkanes of mid-range volatility, and also with reference to squalane ($C_{30}H_{62}$), which is representative of highly involatile alkanes.

Keywords: lagging fires, spontaneous ignition, ignition criteria

INTRODUCTION

The practical motivation for this paper relates to an understanding and interpretation of the conditions at which spontaneous ignition may occur when a flammable liquid penetrates an insulation material surrounding a hot pipe, the so-called "lagging fire". The problem has received relatively little attention, either through theory or through systematic experimental investigation (Lindner and Seibring (1), Bowes and Langford (2), Gugan (3), Bowes (4), Britten (5), McIntosh *et al* (6)). The basic mechanism for the combustion instability that leads to a lagging fire is similar to that for thermal ignition (Frank-Kamenetskii (7), Gray and Lee (8)), namely encompassing the imbalance between the heat release rate with its dependence on temperature and the heat transport rate within the system or away from its surface by conduction and convection. Supplementary to these are the consequences of movement of the liquid or vapour that permeate the insulation. The fluid may become dispersed over an extremely high internal surface area, and ignition then may result from the exothermic oxidation of the fluid in contact with air within the hot, porous structure. For most processes oxygen is essential for exothermic reaction to occur, and its diffusion or limitation of access, as a result of displacement from the voids of the insulation as the liquid vaporises, may also play a part.

The present study is a combination of experimental measurement and theoretical interpretation. The experiments were designed to distinguish between the behaviour of relatively involatile and highly volatile hydrocarbons when they are dispersed in hot microporous insulation. The practical problem, which relates mainly to asymmetric heating of lagging material which surrounds hot pipe and is exposed to ambient temperature on its external surface, is complicated to interpret experimentally and theoretically (Thomas and Bowes. (9)), and it is important to address these conditions in further developments. The present approach builds on the normal procedures involving "cube tests" in a uniformly heated oven, which are formally adopted in EEC and ASTM tests to determine critical ignition criteria (e.g EC test L2951/ 86, auto-flammability).

Typically, insulation materials are made from glassfibre, mineral wool or amorphous silicate compounds. These materials have different thermal insulation properties and densities, and may present significantly different surface/volume ratios within their structure. All of these factors may have important implications for fire risk. The present experiments and modelling were based on microporous, silicate-based insulation which has an open cellular structure with average cell dimension of less than 0.1 μm.

Since many of the liquids that are susceptible to problems of combustion in hot lagging are hydrocarbon based (such as heat transfer fluids or diesel fuel), the alkanes, n-hexadecane (n-$C_{16}H_{34}$, B Pt 560 K, 287 °C), n-octadecane (n-$C_{18}H_{38}$, B Pt 590 K, 317 °C) and n-eicosane (n-$C_{20}H_{42}$, B Pt 616 K, 343 °C) were investigated as representative volatile hydrocarbons over the temperature range 450 - 500 K, (177 - 227 °C). By contrast, 2,6,10,15,19,23-hexamethyltetracosane (squalane, $C_{30}H_{62}$, B Pt 696 K, 423 °C), was studied as representative of the highly involatile liquid alkanes. The relevance of these choices is shown in a chromatogram obtained by capillary column gas chromatography of diesel fuel doped with squalane (Fig. 1).

The purpose of Figure 1 is to demonstrate the boiling range of the components of a typical diesel fuel, from about 470 K (~ 200°C) for the C_{11} alkanes to about 670 K (~ 400°C) for the C_{24} alkanes. Alkanes are not the only components of diesel fuel, but they are usually predominant. The alkanes are conspicuous as a regular series throughout the chromatogram. Markers are inserted at C_{17} and C_{18}, which refer to the respective isoprenoids appearing as the second peak of each doublet. The carbon number of each of the other n-alkanes can be deduced from these markers. The abscissa is a measure of the retention time on the chromatography column and, since a non-selective capillary column (BP1, Scientific Glass Eng.) was used for the separation, the boiling point of each component is directly proportional to the retention time. Squalane ($C_{30}H_{62}$) is retained longer on the column than the diesel fuel components, indicating that it has a higher boiling point, which was determined experimentally from the retention time (see below).

The reactivity of the alkanes investigated was regarded to be sufficiently similar that differences in their combustion characteristics could be attributed to their respective volatilities. To quantify the behaviour we have determined the critical oven temperature at which thermal runaway is able to occur when each of these hydrocarbons is present in a 5 cm cube of the insulation, thermostatted in an oven. The critical temperature is governed by the respective enthalpy of vaporisation (ΔH_v) and, by implication, the normal boiling point.

The theoretical foundation presented here is derived from thermal ignition theory. The classical, Frank-Kamenetskii criterion for thermal ignition, which is related to the imbalance of the heat release and heat loss rates by thermal conduction, represents one extreme of behaviour. It would appear that, to date, virtually all experimental and theoretical studies of the lagging fire problem have been confined to this limit (Brindley *et al* (10). However, as the volatility of the fluid becomes greater, a criterion based on the imbalance between the rates of heat release and evaporation of the fluid becomes more appropriate. The foundations for this new criterion, the transition from the classical thermal ignition to the evaporative criterion, and the relationship between theory and experiment are the subjects of the present paper.

THEORETICAL MODEL AND SAFETY CRITERIA

In this section we develop the theoretical background and the limiting criteria for safe operation, and we discuss the magnitudes of the parameters that may be used to compare theory with experiment. The theoretical model has been cast in such a way as to retain analytical tractability. This means that the representation of certain features which would be appropriate from a both physical and chemical points of view, has to be restricted to simplified forms (Brindley *et al* (11)). For example, the overall chemistry is assumed to be a first order exothermic reaction, as in thermal ignition theory (Bowes (2), Frank-Kamenetskii (7), Gray and Lee (8)). However, there are concerns that it is too simplistic a representation of hydrocarbon combustion, even in a condensed phase (Brindley *et al* (11)). The implications are addressed in the Discussion.

Model and Assumptions

The analytical treatment refers to the geometries which may be represented by a single characteristic dimension, namely the infinite cylinder, the infinite slab and the sphere (Bowes (2), Frank-Kamenetskii (7), Gray and Lee (8)). These are represented respectively in the terms that define thermal and mass diffusion in the conservation equations by the shape factor $j = 0$, 1 and 2. The following assumptions are made.

(i) Reactant is adsorbed in the liquid state on the pore surface within the insulation matrix. It may react in this condensed state or it may evaporate, the vapour being assumed to be inert. There is no inhomogeneity of the surface sites.
(ii) Exothermic oxidation occurs by reaction between gaseous oxygen in the pores and the condensed reactant, with exothermicity Q. In order to link with classical thermal ignition theory, this is interpreted as a single step reaction which is first order with respect to the gas-phase oxygen concentration and the condensed fluid density. The rate constant has an exponential dependence on temperature, with activation energy E.
(iii) Vaporisation is related to the condensed fluid density, and its temperature dependence is controlled by the enthalpy of vaporisation (ΔH_v), expressed in an Arrhenius-like exponential form ($E_v = \Delta H_v$)
(iv) Conductive heat transfer (coefficient λ) and oxygen diffusion (coefficient D_o) are assumed to occur in accordance with Fourier's and Fick's laws respectively. Convective heat transport of gaseous components is ignored, as are pressure gradients within the matrix.
(v) There is no resistance to heat transport at the surface $B_i = \infty$).
(vi) A known amount of fluid is soaked uniformly within the block of insulation initially and there is air present throughout the porous structure, as measured previously (Brindley *et al* (11)).

The model variables, each expressed as a function of spatial coordinate r and time t, are the matrix temperature T(r,t), the molar density of condensed reactant X(r,t) and the concentration of oxygen Z(r,t). The respective conservation equations are thus

$$\frac{\rho c \partial T}{\partial t} = \underset{\substack{\text{chemical heat}\\ \text{release rate}}}{Q A X Z e^{\left(\frac{-E}{RT}\right)}} - \underset{\substack{\text{endothermic}\\ \text{vaporisation rate}}}{Q_V F X \exp^{\left(\frac{-E_v}{RT}\right)}} + \underset{\substack{\text{thermal conduction}\\ \text{rate}}}{\lambda\left(\frac{\partial^2 T}{\partial r^2} + \frac{j \partial T}{r \partial r}\right)} \qquad (1)$$

$$\frac{\partial X}{\partial t} = \underbrace{-AXZ\exp^{\left(\frac{-E}{RT}\right)}}_{\text{chemical consumption rate}} - \underbrace{FX\exp^{\left(\frac{-E_V}{RT}\right)}}_{\text{evaporative loss rate}} \tag{2}$$

$$\frac{\partial Z}{\partial t} = \underbrace{-\nu AXZ\exp^{\left(\frac{-E}{RT}\right)}}_{\text{oxygen consumption rate}} + \underbrace{D_O\left(\frac{\partial^2 Z}{\partial r^2} + \frac{j\partial Z}{r\partial r}\right)}_{\text{oxygen diffusion rate}} \tag{3}$$

With relatively light loadings of fluids, the volumetric heat capacity (ρc) may be assumed constant and represented by that of the inert matrix. The oxygen consumption rate in eq. (3) includes a stoichiometric coefficient ν for the relative numbers of moles of oxygen consumed per mole of fuel reacted.

Non-dimensionalisation of Equations and Reduced Parameters

To facilitate analytical interpretations and to generalise the predicted behaviour, it is appropriate to non-dimensionalise equations (1) - (3). The characteristic time is based on the Fourier time t_F ($= l^2\rho c/\lambda$). Temperature is non-dimensionalised with respect to the temperature coefficient for the chemical reaction (E/R) and given as u (Gray and Wake (12)). By contrast to the more common Frank-Kamenetski parameter ($\theta = E\Delta T/RT_a^2$) (Frank-Kamenetskii (7), Gray and Lee (8)), or $n = T/T_a$ (Aris (13)) this means that T_a (or u_a) can be used as an independent control parameter to explore the properties of the system. The species are non-dimensionalised with respect to the initial molar densities of the uniformly distributed fluid (X_0) and the initial oxygen concentration within the insulation block (Z_0), which is taken to be the same as the external oxygen concentration. Thus the non-dimensionalised terms and reduced parameters are

$$\tau = \frac{t}{t_F}, \qquad u = \frac{RT}{E}, \qquad x = \frac{X}{X_0}, \qquad z = \frac{Z}{Z_0}, \qquad \beta = \frac{E_V}{E},$$

$$q = \frac{QX_0R}{\rho cE}, \qquad q_V = \frac{\Delta H_V X_0 R}{\rho cE}, \qquad a_1 = AZ_0t_F, \qquad a_2 = \frac{\nu X_0 a_1}{Z_0}, \qquad f = Ft_F.$$

The dimensionless exothermicity q is equal to the dimensionless adiabatic temperature excess following complete consumption of the reactant in the absence of any vaporisation. Similarly q_v is equal to the dimensionless temperature decrease owing to complete vaporisation of the reactant with no reaction. The Lewis number, which represents the ratio of oxygen diffusion to thermal diffusion, is given by

$$L_O = \frac{D_O\rho c}{\lambda}$$

Equations (1) - (3) may then be represented in the non-dimensionalised and reduced forms

$$\frac{\partial u}{\partial \tau} = q a_1 x z \exp\left(\frac{-1}{u}\right) - q_V f x \exp\left(\frac{-\beta}{u}\right) + \frac{\partial^2 u}{\partial \xi^2} + \frac{j \partial u}{\xi \partial \xi} \tag{4}$$

$$\frac{\partial x}{\partial \tau} = -a_1 x z \exp\left(\frac{-1}{u}\right) - f x \exp\left(\frac{-\beta}{u}\right) \tag{5}$$

$$\frac{\partial z}{\partial \tau} = -a_2 x z v \exp\left(\frac{-1}{u}\right) + L_0\left(\frac{\partial^2 z}{\partial \xi^2} + \frac{j \partial z}{\xi \partial \xi}\right) \tag{6}$$

Stationary State Solutions and Limiting Conditions

This system of equations must be reduced to one variable for the purpose of analytical interpretation. Following thermal ignition theory, it is necessary to assume that there is always sufficient oxygen and fuel present in subcritical conditions so that both $\partial x/\partial t$ and $\partial z/\partial t$ are assumed to be zero. The behaviour of the system is then governed solely by the energy conservation equation (4). We have shown elsewhere that $\partial z/\partial t = 0$ is a robust criterion but, in practice, $\partial x/\partial t = 0$ cannot always be sustained (Brindley *et al* (11)). Nevertheless, as shown later, the assumption $\partial x/\partial t = 0$ leads to a critical criterion that errs on the side of safe operation.

From eq (4) there are two limiting physical conditions for a lagging fire to develop. The first is that of a fluid which is sufficiently involatile at the critical temperature that its behaviour resembles thermal ignition under Frank-Kamenetskii conditions (Frank-Kamenetskii (7)). Most examples of lagging fires that have been studied so far in the laboratory appear to approach this extreme (Bowes and Langford (2), Britton (5)). This condition may be represented as a stationary state solution to eq (4) in the limit of no evaporation (McIntosh *et al* (14)). That is,

$$\frac{\partial u}{\partial \tau} = q a_1 x z \exp\left(\frac{-1}{u}\right) + \frac{\partial^2 u}{\partial \xi^2} + \frac{j \partial u}{\xi \partial \xi} \tag{7}$$

Invoking the Frank-Kamenetskii exponential approximation (Frank-Kamenetskii (7)) and assuming constant x and z, equation (7) may be solved in one dimension to give the classical solution

$$\delta_{cr} = \frac{q a_1 x z}{u_{FK}^2} \exp\left(\frac{-1}{u_{FK}}\right) = \frac{Q A E X_0 Z_0 l^2}{\lambda R T_{FK}^2} \exp\left(\frac{-E}{R T_{FK}}\right) \tag{8}$$

The Frank-Kamenetskii parameter, δ_{cr}, takes the values 0.878, 2.00 and 3.32 at the critical dimensionless ambient temperature u_{FK} or, in dimensional form, T_{FK}, for the shape parameters j = 0 1 and 2. An equivalent harmonic mean square radius (R_0) can be defined for any given stellate shape (Boddington *et al* (15)), which, for a cube, yields j = 3.28 and $\delta_{cr}(R_0) = 3.665$ at $Bi = \infty$.

The second limiting condition arises when the volatility of the fluid is sufficiently high that the propensity for thermal runaway is controlled entirely by an interaction between the chemical heat release rate and the endothermic evaporation rate (McIntosh *et al* (14)). This condition can also be interpreted from a stationary state solution of eq (4) involving only the first and second terms on the right hand side. Thus, if x and z are assumed constant, a dimensionless critical temperature (u_{cr}) can be derived, in the analytical form

$$u_{cr} = \frac{1-\beta}{\ln(q a_1 z / q_v f)} \tag{9}$$

For $u < u_{cr}$, the system is net endothermic and is not subject to any temperature rise. This represents one extreme for an inherently safe system. Hitherto, the relevance of evaporation as a controlling factor and the conditions at which it becomes important seem not to have been addressed in a formal way.

There is a switch from u_{FK} to u_{cr} as the more appropriate criterion for safe operation as the volatility of the fluid increases, and this occurs at a dimensionless ambient temperature for the transition, u_a^*. Numerical predictions of the dependence of u_{FK}, u_{cr} and u_a^* on the parameters of the combustion system are discussed elsewhere (Brindley *et al* (14). However, the conditions that are appropriate for a switch from u_{FK} to u_{cr} are given by a transcendental relationship between the principal quantities, derived as follows from an equality of equations (8) and (9):

$$\frac{(1-\beta)^2}{\ln\left(\dfrac{q^* a_1^* z^*}{q_v^* f^*}\right)} \; \frac{1}{(q_v^* f^*)^{(1/(1-\beta))}} \; \frac{1}{x}(q^* a_1^* z^*)^{(\beta/(1-\beta))} = \frac{1}{\delta_{cr}} \tag{10}$$

where * signifies the values taken at the crossing point.

Although eq. (10) may be modified to make a specific parameter the subject of the formula, the dimensionless enthalpy of vaporisation at which the transition occurs (q_v^*), which would be of greatest interest in the present work, cannot be expressed in an explicit analytical form. The major difficulty arises because β is a function of q_v^*. The dependence of u_{cr} on q_v, and that of its fully dimensional counterpart ΔH_v, and the relationship to u_{FK} are discussed further below.

Thermochemical and Kinetic Parameters and Comparison with Experiment

Fluids that are encountered in lagging fires are often hydrocarbon based, so the -CH2- moiety may be regarded to be a representative part of the chemical structure. Its complete oxidation is given by

$$\text{-CH}_2\text{-} + 3/2\ \text{O}_2 = \text{CO}_2 + \text{H}_2\text{O} \tag{11}$$

Whilst the overall heat of combustion (Q) is 4.4×10^7 J kg^{-1} of the reactant, most of this energy is released in the late stage of reaction. This is preceded by many competitive and consecutive, free radical chain propagation and branching processes, which lead to complex mixtures of partially oxidised or degraded intermediates prior to the formation of the final products (Griffiths (16)). The onset of spontaneous ignition of hydrocarbons is known to evolve at low temperatures (T < 700 K, ~ 430 °C)) through organic peroxides and other partially oxygenated intermediates. Thus the exothermicity associated with the preliminary stage should be used to represent Q in determining the critical criteria for spontaneous ignition and not the overall heat of combustion. The partial oxidation of $-CH_2-$ might be take either of the forms

$$-CH_2- + 1/2\ O_2 = CO + H_2 \tag{12}$$

or

$$-CH_2- + 1/2\ O_2 = CH_2O\ . \tag{13}$$

for which the exothermicity of reaction is approximately 6.5×10^6 J kg^{-1} in each case. This is a relatively small proportion of the overall heat of combustion. In the present calculations Q is taken to be 2.5×10^6 J kg^{-1}. in order to allow for the still lower exothermicity associated with peroxide formation, which cannot be interpreted directly from $-CH_2-$ oxidation.

The activation energy associated with peroxide forming processes may be expected to be in the range 150 - 200 kJ mol^{-1} (Snee and Griffiths (17)). The representation of the chemistry as a single step, first order reaction requires the pre-exponential factor (A or a_1) to be obtained empirically. This parameter was derived in the present work by matching the critical temperature obtained for squalane at $\delta_{cr} = 3.665$. Kinetic and thermal parameters are summarised in Table 1.

Vaporisation Characteristics

The fluid vaporisation rate, expressed in a form related to the Clausius - Clapeyron equation for the temperature dependence of the vapour pressure of liquids, means that the enthalpy of vaporisation determines not only the endothermicity of the vaporisation process but also the temperature coefficient for the rate at which the vapour is generated. The temperature coefficient is expressed as an activation energy for the vaporisation process (E_v) in Table 1.

The enthalpies of vaporisation of the n-alkanes studied in this work fall in the range 55 - 70 kJ mol^{-1}. From the normal boiling. point of squalane obtained from Fig. 1, ΔH_v for squalane is about 85 kJ mol^{-1}. The measured boiling point, 696 (± 1) K (or 423 °C), seems more reasonable than that quoted in the Merck Index (18), 623 K (or 350 °C), which (when combined with other vapour pressure data) leads to the unreasonably high value $\Delta H_v = 135$ kJ mol^{-1}. The empirical factor F, representing the vaporisation rate coefficient, relates to the surface area within the porous structure as well as the molecular behaviour of the liquid itself, and so this was derived from comparisons with the combustion measurements made by McIntosh et al (6).

Table 1: Physical and chemical parameters related to the comparisons between theory and experiment

Exothermicity Q / J kg^{-1}	2.34×10^6
Enthalpy of vaporisation Q_v / J kg^{-1}	$(2.0 \pm 0.1) \times 10^5$
Pre-exponential factor (reaction) A / kg^{-1} m^3 s^{-1}	1.5×10^{13}
Pre-exponential factor (vaporisation) F / s^{-1}	5.8×10^3
Activation energy (reaction) E / J mol^{-1}	1.5×10^5
Activation energy (vaporisation) E_v /:J mol^{-1}	$(5.0 - 8.0) \times 10^4$
Oxygen diffusion coefficient D_0 / m^2 s^{-1}	1.0×10^{-5}
stoichiometry coefficient ν	0.3

EXPERIMENTAL STUDIES

Experiments were performed by dispersing the liquid (10 cm^3) within a 5 cm cube of an amorphous silicate (micropore, matrix density 360 kg m^{-3}). An even distribution was ensured by dissolving the liquid in diethyl ether (50 cm^{-3}) and allowing this solution to soak through the block. The solvent was then allowed to evaporate completely at laboratory temperature before an experiment was started. A thermocouple (T_1/T_2, 0.1 mm dia wire) was located at the centre of the cube with a reference junction located external to the surface, so that the difference between the centre and the ambient (oven) temperature could be recorded as a function of time using a recorder.

For the purpose of mass loss measurements, a cube was suspended by wire from the arm of a torsion balance so that it was located, via a small entry port, at the centre of a recirculating air oven (void volume 0.25 m^3). Mass changes were recorded manually as the oven was heated up from laboratory temperature and stabilised at its pre-set value.

Oxygen was detected by continuous sampling to a mass spectrometer (RGA 10, magnetic sector instrument giving unit mass separation to 100 a.m.u.) via a silica microprobe (50 μm i.d.) inserted to the centre of the block and connected to the mass spectrometer by a heated stainless steel tube (0.5 mm i.d.). The pumping rate through the probe and the pressure drop to the mass spectrometer operating pressure (~ 10^{-6} mbar) were controlled by a two-stage pumping system with the intermediate pressure at the first stage being controlled by a needle valve, at approximately 4 mbar. Most of the pressure drop in the sampling line took place at the microprobe tip, so that quenching of the gaseous fraction occurred virtually instantaneously. Extensive tests were performed to optimise the mass spectrometer response whilst minimising the perturbation of the system by continuous sampling. The oxygen concentration was determined from the intensity of the mass peak at m/e = 32 relative to the background peak in the absence of oxygen, without further correction for other contributing species. Corrections were made for variations of the sampling rate as a consequence of temperature changes at the probe, which affected the viscosity of the gaseous sample. The mass spectrometer measurements were made by a repetitive scanning of the m/e range 29 - 33 over a period of one minute. This ensured that the maximum intensity of the m/e = 32 peak could be obtained repeatedly at regular intervals throughout the duration of an experiment (< 3 hours). The statistical variation in the peak height from successive scans was ± 5%. Temperature measurements were made simultaneously with the determination of oxygen concentrations, as described above. A different oven was used for the measurement of oxygen concentrations than that used for mass loss measurements, and it was necessary to use a different microporous block in these separate experiments.

EXPERIMENTAL RESULTS

Studies of Squalane Combustion

The critical oven temperature at which spontaneous ignition of squalane (10 cm^3) in a 5 cm cube was found to be 478 ± 1 K, 205 ± 1 °C (Table 2). Temperature change and oxygen concentration measurements during the combustion of squalane within the insulation at a supercritical oven temperature of 485 K are shown in Fig. 2. The average mass loss rate of liquid squalane from prior to onset of the hot stage of ignition was approximately 0.3 g per hour which is consistent with its vapour pressure at the oven temperature (4 - 5 mbar over the range 480 - 490 K, *ca.* 210 - 220 °C).

Ignition took place within the cube, at 485 K (7 K above criticality), at about 90 minutes after the experiment was begun (Fig. 2). There was an initial phase during which the block responded to the ramping and stabilisation of the oven temperature. This was recorded as an initial negative temperature difference resulting from the slower response of the centre of the cube with respect to the rising oven temperature. An equality between the centre temperature and the external temperature was reached after about 50 minutes. There then followed a period during which a further temperature rise at the centre occurred during which ΔT reached 50 K over an interval of about 10 minutes. In the subsequent development following an inflexion in the record, the centre temperature rose to nearly 500 K above that of the oven.

There was no depletion of oxygen at the centre of the insulation material throughout virtually the whole of the heating period and its concentration was still about half of the initial value even when the centre temperature had risen by more than 50 K above that at the edge. Complete consumption of oxygen at the centre of the block occurred just prior to the attainment of the maximum temperature. Undoubtedly reaction within the block had become oxygen diffusion controlled by this stage. A rapid recovery of the oxygen to its initial concentration occurred once the maximum temperature had been reached. It is possible that the inflexion of the thermal record in Fig. 2 may be associated with oxygen diffusion control but complex chemistry may also be contributory, such as the burn-out of carbonaceous residues once the centre temperature has become sufficiently high for this to take place.

The Combustion of Evaporation of Higher Volatility Alkanes

The behaviour of the alkanes n-$C_{16}H_{34}$, n-$C_{18}H_{38}$ and n-$C_{20}H_{42}$, and that of squalane ($C_{30}H_{62}$) is summarised in Table 2. The dimensionless critical temperature (u_{cr}) is derived from an activation energy of 150 kJ mol^{-1}. As indicated in the comments in Table 2, whereas n-eicosane (n-$C_{20}H_{42}$) showed a clear distinction between a limited extent of self-heating and fully-developed high temperature combustion ($\Delta T \sim 500$ K), n-hexadecane (n-$C_{16}H_{34}$) was capable of exhibiting only a very small temperature rise at the centre of the cube accompanying its evaporation at all oven temperatures up to its normal boiling point. This is illustrated in Fig. 3 at an oven temperature which is close to the boiling point of n-hexadecane (560 K).

Table 2: Combustion of selected alkanes in hot insulation experiments

Alkane	B Pt / K	T_{crit} / K	u_{cr}	Comment
2,6,10,15,19,23-hexamethyltetracosane, $C_{30}H_{62}$	696	478 ± 1	0.0265	no significant evaporation
n-eicosane, n-$C_{20}H_{42}$	616	505 ± 2	0.0280	clearly defined criticality
n-octadecane, n-$C_{18}H_{38}$	590	523 - 528	0.0291	marginal criticality
n-hexadecane, n-$C_{16}H_{34}$	560	-	∞	marginal self-heating only, no ignition

The behaviour of n-octadecane (n-$C_{18}H_{38}$) was intermediate between the lower and higher molecular mass alkanes. It exhibited a quite strong "parametric sensitivity" over the oven temperature range 513 - 528 K (Fig. 4). However, even at much higher oven temperatures the centre temperature excess did not exceed 100 K, as shown in Fig. 3. Mass loss measurement during the combustion of n-octadecane at 528 K shows that virtually all of the fluid had evaporated before significant extents of self-heating occurred (Fig. 4). Clearly a limitation on the residual fuel restricts the rate and extent of heat release during thermal runaway.

DISCUSSION

One practical consideration that emerges from this work is the experimental observation that, in general, alkanes may become susceptible to spontaneous ignition in insulation materials at relative molecular mass in the range 218 - 246. Other classes of organic compounds may have similar reactivity, especially if they have long alkyl side-chains. However, their volatility (reflected in their boiling points) may be quite different, and this must be taken into account when considering the hazard implications. For this reason it is important to formalise the criteria for criticality and ignition.

Relationship Between Theory and Experiment

Whereas the theory has been developed here on the basis of spherical symmetry, the experiments were performed in cubes of material. From both theoretical and experimental points of view there is no qualitative distinction between spontaneous ignition which occurs in cubes (or other axisymmetric shapes) and in spherically symmetric systems, and the criteria for criticality in a cube can be interpreted in a quantitative way from that in a sphere (Boddington *et al* (15), Beever and Griffiths (19), Jones and Puignou (20)). Moreover, at marginally subcritical conditions, spontaneous combustion evolves from the centre of the cube with virtually spherical symmetry. It is only when the temperature begins to rise in regions close to the surfaces that a distortion evolves as a consequence of the reduced thermal gradient along the axis into the corners relative to that perpendicular to the faces of the cube (Beever and Griffiths (21)).

Using the criteria of Boddington *et al* (15), we have derived the dimensionless critical temperature (u_{cr}) from the experimental result in terms of the Frank-Kamenetskii equivalent sphere (Table 2), so that comparisons may be made with the theoretical values of u_{FK} and u_∞ as the enthalpy of vaporisation increases (Fig. 5). Both of the theoretical criteria err to the safe side with respect to the critical conditions for- the volatile alkanes in the range C_{16} - C_{20}, and the crossing point of u_∞ with u_{FK} coincides well with the departure of criticality of the more volatile fluids from the u_{FK} line. The more satisfactory theoretical criterion for safe operation then becomes the condition for u_∞. However, u_∞ exists even for fluids of sufficiently low enthalpy of vaporisation (or normal boiling point) that the fluid evaporates before exothermic reaction can develop. This discrepancy arises from the analytical constraint set by the assumption that $\partial x/\partial t = 0$, which signifies that there is no reactant loss. Whilst the chemical oxidation rate may be very slow (so that the condition $\partial z/\partial t = 0$ remains valid), in reality the evaporation rate becomes too high for the reactant density to remain even approximately constant. According to the data in Fig. 5, it would be extremely useful to establish a theoretical relationship which could give a prediction of the asymptotic limit for criticality that is demonstrated experimentally by n-$C_{16}H_{34}$.

Scaling Relationships and Assessment of Hazards Associated with Asymmetrically Heated Systems

When tests are performed in uniformly heated systems, and it is found that the classical ignition criterion (u_{FK}) is appropriate to a particular fuel, the conditions for safe operation may be interpreted from the rules established by Boddington *et al* (15) for a wide range of shapes at any size. These rules have been validated by experiment (Beever and Griffiths (19), Jones and Puignou (20), Egeiban *et al* (22)). Appropriate kinetic and thermal parameters are required for the chemical system, which can be derived from a series of experiment in cubes of different size if the parameters are not already known (Bowes (4), Beever and Griffiths (19)), Jones and Puignou (20)). Whether or not u_{FK} or u_{x} is the most appropriate criterion is determined by u_a^*, which is derived through equation (10). When u_{x} is relevant, the conditions for safe operation rest entirely on the relationship between the exothermic oxidation rate and the endothermic evaporation rate.

The simplest analytical form for u_{x}, equation (9), contains the empirical, dimensionless evaporation coefficient, f, which also relates to the surface area, porosity and transport of the vapour from the inert matrix (Brindley *et al* (10)). The properties of insulation and of the fluid can be separated in a more sophisticated formulation if the prediction of criticality in a different type of insulation material is to be made (Brindley *et al* (11)). However, this analysis is amenable only to numerical interpretation as yet because a fourth equation must be included to represent the vapour of the fluid and its transport through the material. The physical representation is of an interconnected pore structure with the possibility of multilayer build-up of liquid on the pore surface. The vapour density adjacent to the surface is at equilibrium with the liquid at the local surface temperature. The vapour density at the centre of the pore is governed by the diffusion gradient between it and the pore surface, such that evaporation and condensation are admitted, and also between the interconnecting pores and the external environment (Brindley *et al* (11)).

The conditions that relate to the classical imbalance between the heat release and heat loss rate in an asymmetrically heated system have been addressed by Thomas and Bowes (9). When evaporative loss becomes a controlling factor of spontaneous ignition in an asymmetrically heated system, an analytical criterion cannot be defined in a simple form, as is the case for uniform heating. Difficulty arises because the there is always a propensity for evaporation to take place at the hot surface, which may result in re-condensation in a cooler region of the insulation material. Thus the location of the seat of ignition may have a spatial dependence governed lay the thermal gradient and the diffusion characteristics throughout the system. These complicated but extremely interesting interactions are under further investigation.

Chemical Features of the Theoretical Model

The high non-linear nature of the temperature excursion in the experiments performed on squalane during ignition (Fig. 2) is not characteristic of that exhibited either theoretically or experimentally in a classical thermal ignition (Griffiths and Scott (23)). It is reminiscent of the branching chain - thermal interactions that occur during hydrocarbon oxidation both in gas and liquid phases (Griffiths and Scott (23)). Consequently the representation of the combustion chemistry in reactions of these kinds as a single step first order exothermic reaction may not be adequate. Also there is a potential difficulty with regard to reaction of the condensed phase expressed as a conventional concentration dependence. Whilst it is not practical in the present context to address a detailed kinetic model there has been an extensive development of reduced kinetic models to interpret the spontaneous ignition of hydrocarbons (Griffiths (16)). One possibility is to regard the chemistry to be represented as a quadratic branching process with allowance for reaction at the surface in the reduced form

$$v=kxZ\,\{(Z_0-Z)+\zeta\}. \qquad (14)$$

The term x represents the effective reaction density of the adsorbed liquid which is related to the Langmuir adsorption isotherm $x = X/(X_m + X)$ where X_m represents the monolayer coverage and X is the local density. Until the monolayer is exposed the oxidation rate depends only on the number of adsorption sites occupied by the liquid and not on the remaining adsorbed liquid density. Z_0 and Z represent the gaseous oxygen density initially and at time t respectively. The *small parameter ζ is an initiating term ($\zeta << (Z_0 - Z)$) and is essential to permit the autocatalytic* reaction to begin. The inclusion of ζ represents a seeding of the system with a small amount of the degenerate branching agent rather than it being generated in an initiation reaction (Gray and Scott (24)). The expression for quadratic autocatalysis has been shown to be appropriate for gas-phase oxidation where there is a large excess of fuel. The acceleration in the reaction rate is then independent of the fuel concentration but is a function of the oxygen concentration (Griffiths and Phillips (25)). The properties of this kinetic representation for reaction of hydrocarbons in hot lagging have been discussed elsewhere (Brindley *et al* (11)).

Anomalous Behaviour Observed in Laboratory Experiments

Our experiments are similar in design to those performed by Britton (5) in 1991. However, most of the fluids studied by him (amines, olamines and glycols) were reactive at fairly low temperatures and they had comparatively high boiling points, so the competition between reactivity and volatility was not put to rigorous test in that particular study. The corresponding behaviour in the present work is shown by squalane (Fig. 2). The longest ignition delay that we were able to reproduce for squalane in a uniformly heated 5 cm cube was about 7 hours. This time is entirely consistent with that which would be expected from the imbalance of the heat release and heat transport rate by thermal conduction at marginally supercritical conditions (Brindley *et al* (11)).

In some of Britton's experiments ignition delay times were recorded which exceeded 10 hours, and for the glycols these times extended to several days. In our own studies on a series of normal alcohols (McIntosh *et al* (6)), we also recorded ignition delays that exceeded 24 hours. Delays of this duration are incompatible with the thermal relaxation times for a 5 cm cube of any insulation material. Moreover, mass loss measurements involving the alcohols showed that there was a residual fraction of alcohol retained within the insulation matrix long after the normal evaporative process should have reached completion.

The substances involved in these abnormal cases tend to be polar in character. We believe that exceptionally strong adsorption forces may have been involved in the adhesion to the surface, which then controlled the development and eventual occurrence of ignition. Hydrogen bonding of the substrate to the silicate based insulation is one example of how adhesion may have been brought about. This implies that in certain circumstances, the normal expectation that evaporation will reduce the potential hazard of a fluid in hot insulation is not appropriate. The enhanced risk of *fires developing for reasons connected with this anomalous must be taken into account. These* aspects of the lagging fire problem require further investigation.

ACKNOWLEDGEMENT

The authors gratefully acknowledge financial support of this project from EPSRC (GR/J27431). Thanks are due also to B. Frere for the chromatography shown in Figure 1 and the boiling point determination of squalane.

REFERENCES

1. Lindner, H. and Seibring, H. 196,, Chemie-Ing. Tech., 39:667 - 671
2. Bowes, P.C. and Langford, B. 1968, Chem. and Proc. Eng., 49: 108 - 116
3. *Gugan, K., 1974, I. Chem. E. Symp. Ser., 39: 28 - 43*
4. Bowes, P.C., 1984, Self-heating: evaluating and controlling the hazard, Her Majesty's Stationery Office, London
5. Britton, L.G., 1990, Plant / Operations Prog..AIChE, 10: 27 - 37
6. McIntosh, A.C., Bains, M., Crocombe, W. and Griffiths. J.F.. 1994, Combust. Flame, 99: 541 - 550
7. Frank-Kamenetskii, D.A., 1969, Diffusion and Heat Transfer in Chemical Kinetics (trans. J.P. Appleton) Plenum Press, New York
8. Gray, P. and Lee, P.R., 1968, Oxidation and Combustion Reviews, vol 2, ed C.F.H. Tipper, Elsevier, Amsterdam, 1 - 94
9. Thomas, P.H. and Bowes, P.C., 1961, Trans. Faraday Soc., 57:2007 - 2017
10. Brindley, J., Griffiths, J.F., Hafiz, N., McIntosh, A.C. and Zhang, J., 1998, AIChE Journal, 44: 1027 - 1037
11. *Brindley, J., Griffiths, J.F., McIntosh, A C. and Zhang, J., 1998, Twenty-Seventh* Symposium (International) on Combustion, The Combustion Institute, in press
12. Gray B.F and Wake G.C., 1988, Combust. Flame, 71: 101 - 104
13. Aris, R., 1975, The Mathematical Theory of Diffusion and Reaction in Permeable Catalysts, Clarendon Press, Oxford
14. McIntosh, A.C., Truscott, J.E., Brindley, J., Griffiths, J.F. and Hafiz, N., 1996, J. Chem. Soc. Faraday Trans., 92: 2965 - 2969
15. Boddington, T., Gray, P. and Harvey, D.I., 1971, Phil. Trans. R. Soc. Lond., A270: 467 - 506
16. Griffiths, J.F., 1995, Prog. Energy Combust. Sci., 21:25 - 107
17. Snee, T.J. and Griffiths J.F., 1989, Combust. Flame, 75: 381 - 395
18. The Merck Index, 11th Edition, 1989, Merck and Co. Inc., Rahway, N.J.
19. Beever, P.F. and Griffiths, J.F., 1989, International Symposium on Runaway Reactions, CCPS, AIChE, New York, 1 - 20
20. *Jones, J.C. and Puignou, A., 1998, Trans. Inst. Chem. Eng. Part B: Process Safety and* Environmental Protection, 76: 14 - 18
21. Beever, P.F. and Griffiths, J.F., unpublished results
22. Egeiban, O.M., Mullins, J.R., Scott, S.K. and Griffiths, J.F., 1982, Nineteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, 825 - 833
23. Griffiths, J.F. and Scott, S.K., 1987, Prog. Energy Combust. Sci., 13, 161 - 191
24. Gray, P. and Scott, S.K., 1990, Chemical Oscillations and Instabilities, Clarendon Press,Oxford
25. Griffiths, J.F. and Phillips, C. H., 1989, J. Chem. Soc. Faraday Trans. I, 85: 3471 - 3479

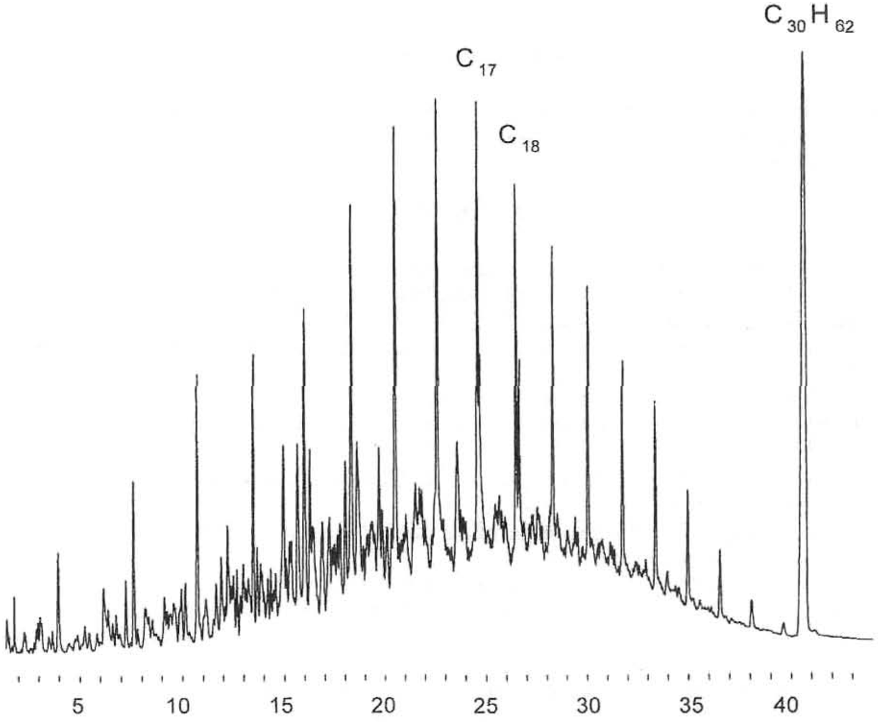

Figure 1 A chromatogram of a typical diesel fuel doped with squalane ($C_{30}H_{62}$),. The sample was separated on a 12 m BP1 capillary column temperature programmed from 50 to 250 °C for 40 minutes at 5 °C per minute. The ordinate represents the peak intensity, which is proportional to the amount of each component . The abscissa is marked with time of elution, in minutes, which is proportional to the boiling point of each component. The most prominent peaks are the series of n-alkanes, n-$C_{17}H_{36}$ and n-$C_{18}H_{38}$ being identified from the corresponding isoprenoids which appear as the second peak of each doublet.

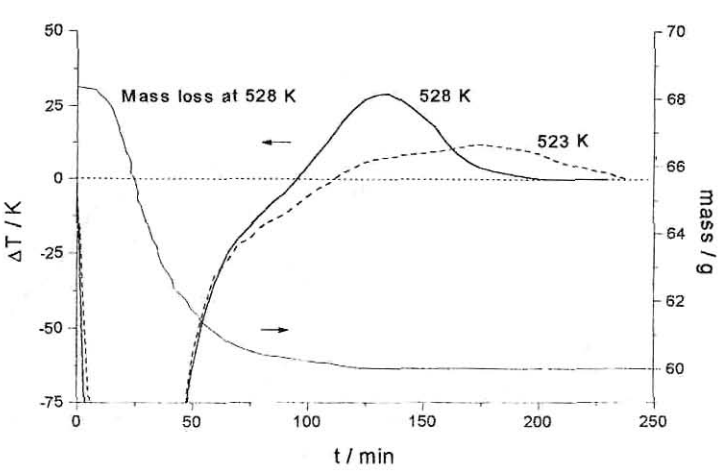

Figure 4 Temperature change at the centre of a 5 cm cube of microporous insulation during the combustion of n-$C_{18}H_{38}$ at oven temperatures of 523 and 528 K (250 and 258 °C). The measured mass loss of fluid at 528 K is also shown.

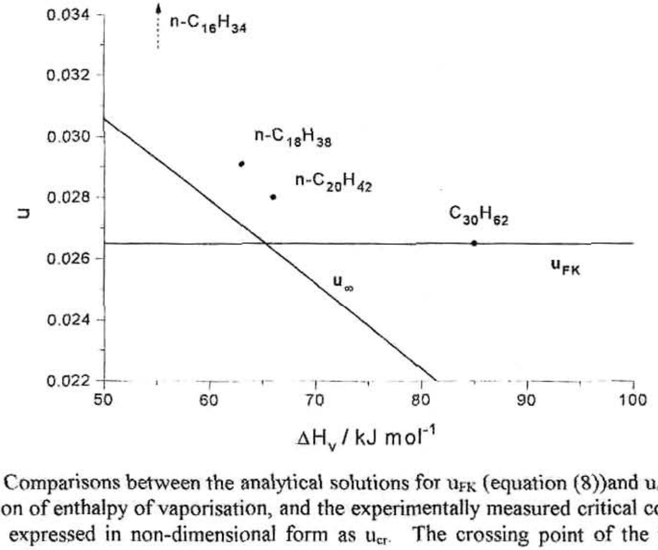

Figure 5 Comparisons between the analytical solutions for u_{FK} (equation (8))and u_{∞} (equation (9)), as a function of enthalpy of vaporisation, and the experimentally measured critical conditions for the n-alkanes, expressed in non-dimensional form as u_{cr}. The crossing point of the theoretical lines represents u_a*.

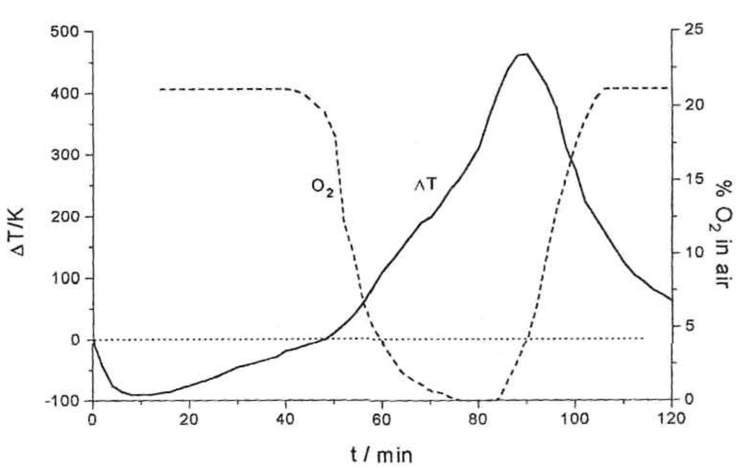

Figure 2 Temperature change and oxygen concentration measured at the centre of a 5 cm cube of microporous insulation during the course of the development of spontaneous ignition of squalane at an oven temperature of 485 K (212 °C).

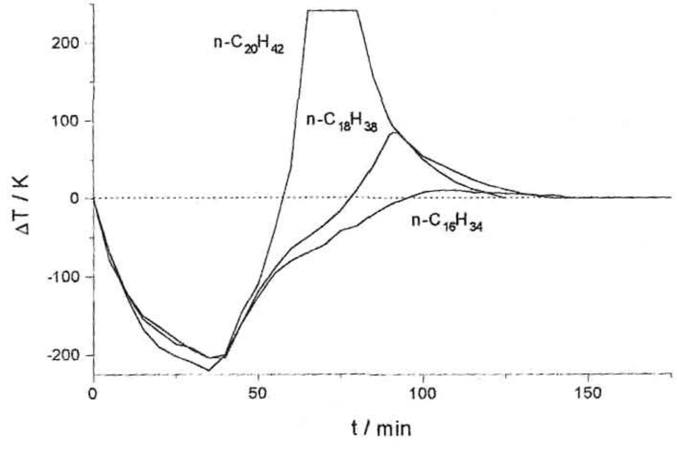

Figure 3 Temperature change at the centre of a 5 cm cube of microporous insulation, during the combustion of n-$C_{16}H_{34}$, n-$C_{18}H_{38}$ and n-$C_{20}H_{42}$ at an oven temperature of 558 K (285 °C).