Theory and Applications of Ignition with Variable Activation Energy

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The determination of critical conditions for thermal ignition of combustible materials has been traditionally studied by the use of one overall reaction with bounded parameter values for the activation energy and other chemical constants. Significant errors can occur in the values of the threshold parameters for ignition when there are two (or more) simultaneous reactions present with distinct values of the chemical constants. Recent work with simultaneous parallel reactions showed the thresholds for ignition could be lowered in this case. In this paper, motivated by experimental results for forest litter and coal, it is shown that for sequential reactions (different values of parameters in different temperature ranges) that the threshold conditions are changed (safer for lower ambient temperatures and less safe for higher ambient temperatures).

The mathematical analysis is summarised and a detailed analysis is given for the forest litter and crushed coal applications. The experimental results show that variable activation energy does occur and that this extension of the classical Frank-Kamenetskii theory is needed. Here the analysis is confined to the slab geometry only but the ideas developed can easily be extended to more general systems, including those involving mass transport, consumption, and phase changes.

Keywords: thermal ignition, variable activation energy.

INTRODUCTION

The co-existence of two or more exothermic reactions, during a self-heating process, is common. These reactions, if they are parallel reactions, behave more or less similarly at low or high temperature\(^1\). This function may be simplified by a number of discrete activation energies over different temperature ranges. The simplest case occurs when only two different activation energies exist. This regime also applies to the situation where one kind of reaction takes place as temperatures below the threshold temperature and another kind of reaction occurs beyond the threshold temperature. Two examples are given as follows:

1. In the case of self-heating of a low rank coal, as summarised by Berkowitz\(^2\), the initial stages of oxidation are characterised by chemisorption of oxygen at readily accessible surface sites and by formation of acidic functional groups. If moisture is present or is generated from chemically combined hydrogen in the coal, some chemisorbed oxygen will also form peroxide or hydroperoxied complex. Given enough time, oxidation gradually degrades the coal itself, first converting it into alkali soluble, but otherwise still coal-like solids known as humic acids and then breaking those substances down into progressively smaller molecules. Below 343K, oxidation does not proceed much beyond forming acidic functional groups and peroxides. Further oxidation proceeds so slowly that significant concentrations of humic acids develop only after a long period of time. Beyond 343K, peroxides form only transiently or not at all. Rapid generation of humic acids...
occurs only in the range of 423K to perhaps 523K. The moisture content, as witnessed by various researchers, has very different effect on coal oxidation rate at the above two temperature ranges of greater than 343K or less than 343K\[S,4,5\]. Banerjee\[ el measured the activation energies of a number of coals at temperatures from 303K to 443K. His data clearly demonstrate the two-reactivity regime and the threshold temperature was found to vary between 353K and 393K, depending on the nature of coal.

Jones et al\[7,8,9,10\] completed studies on the self-ignition of a number of forest leaves. The two parallel-reaction regime in which the effects of oil content and solid leaf content were considered separately, i.e. the activation energies of both materials were estimated firstly according to the pervious literature and then the overall activation energy was calculated applying the theory of thermal explosion with simultaneous parallel reactions proposed by Boddington et al\[11\] and Graham-Eagle and Wake\[12\]. The predicted overall activation energies of the leaf samples agreed consistently with the experimental data[10]. The reactivity of oil is about 10 times that of the solid leaf. Therefore, the oil contribution becomes more significant at high temperatures. Over wider temperature ranges than that used in the experiments, one should expect an approximate two-reactivity regime to happen for all the samples. In fact, the overall reactivity of an Eucalyptus Saligna leaf has been found to possess this regime over the range of the oven temperatures used.

**FORMULATION**

For simplicity we will formulate this in a slab geometry (so as to use the simple Frank-Kamenetskii theory). It should be noted that the theory developed here, like that in Boddington et al\[11\] works in any shape. The simplest use, when reactant consumption is neglected (often good enough for the commercial investigation) gives in the steady-state

\[k \Delta T + \rho Z \varepsilon \Phi = 0, \quad \text{in the region} \quad (2.1)\]

where, \(k\), \(\rho\), \(Z\), \(E\), \(R\) are the thermal conductivity, density, power density, activation energy and gas constants respectively and \(\Delta T\) is the Laplacian of the spatially distributed temperature \(T\). These parameters are all constant except for the jump in \(Z\) and \(E\) at the threshold temperature \(T_s\) with

\[
Z = \begin{cases} 
Z_1 \quad & E = \begin{cases} 
E_1 \quad & T < T_s \\
E_2 \quad & T > T_s 
\end{cases} 
\end{cases}
\]

The formulation of Frank-Kamenetskii is obtained by letting

\[\theta = \frac{E_1}{RT_s^2} (T - T_s)\]

and using the standard exponential approximation

\[\Delta \theta + \varepsilon \Phi \phi \omega \theta = 0, \quad \text{in the region, when} \quad T < T_s, \quad \text{i.e.} \quad \theta < 0\]

where the Frank-Kamenetskii parameter \(\delta\) is given by

\[\delta = \frac{\rho Z_1 E_1 l^2 \exp(-E_1/RT_s)}{T_s^2 k R}\]  \[(2.2)\]

and \(l\) is the appropriate thickness.

In the higher temperature region we get a similar equation

\[\Delta \theta + \delta \omega \Phi \omega \phi \theta = 0, \quad \text{in the region, when} \quad \theta > 0.\]

Here, \(\omega = E_2/E_1, \phi = Z_2/Z_1\) are the ratios of the appropriate chemical constants (\(\omega = \phi = 1\) is the classical situation).

In the simulations which follow and which stimulated this work, the ignition of aggregates in drying chambers, the region was effectively an infinite slab. So in dimensionless coordinates

\[
\begin{align*}
\frac{d^2 \theta}{dz^2} + \delta \varepsilon \Phi \phi \omega \theta &= 0, \quad \theta < 0 \\
\frac{d^2 \theta}{dz^2} + \delta \omega \Phi \omega \phi \theta &= 0, \quad \theta > 0
\end{align*}
\]

(2.3)

We will take

\[
\begin{align*}
\theta(0) &= \theta_0 \leq 0 \\
\theta(1) &= \theta_1 \geq 0
\end{align*}
\]

(2.4)

which corresponds to the boundary \(x = 0\) being cooler (using ambient temperature) and the other boundary \(x = 1\) being hotter.

In this paper we look at the solution of the problem (2.3), (2.4) for this model and compare experimental evidence/computational results for this model with the classical one.

**ANALYSIS**

The simulations which follow use data from experiments in two models:

1. The classical model when \(Z_1 = Z_2, E_1 = E_2\);
2. The sequential reaction model, \(Z_1 \neq Z_2, E_1 \neq E_2\).

(Equations (2.3), (2.4)).