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Pyrolysis and ignition of a polymer by transient irradiation

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ABSTRACT

Pyrolysis is the thermochemical process that leads to the ignition of a solid fuel and a key mechanism in flame spread and fire growth. Because polymeric materials are flammable and ubiquitous in the modern environment, the understanding of polymer pyrolysis is thus essential to tackle accidental fires. In this paper, we used transient irradiation as an external source of heat to study the process of pyrolysis and ignition of a polymer. While previous ignition studies use constant irradiation, transient irradiation is the most frequent condition found in accidental fires, but it lacks a theoretical framework since it has been ignored in the literature. Moreover, transient irradiation is a more comprehensive case for the understanding of pyrolysis where nonlinear heat transfer effects challenge the validity of solid-phase criteria for piloted ignition developed previously. We propose here that transient irradiation is the general problem to solid fuel ignition of which constant irradiation is a particular case. In order to investigate how this novel heat source influences polymer pyrolysis and flammability, numerical simulations and experiments have been conducted on poly(methyl methacrylate) (PMMA) samples 100 mm by 100 mm and 30 mm deep exposed to a range of parabolic pulses of irradiation. The 1D model, coded in GPyro, uses heat and mass transfer and single-step heterogeneous chemistry, with temperature dependent properties. The predictions are compared to experiments conducted in the cone calorimeter for the constant irradiation and the Fire Propagation Apparatus for transient irradiation. The experiments validate the temperature predictions of the model and also provide the time to ignition. The model then complements the experiments by calculating the mass loss rate. A series of 16 parabolic pulses (including repeats) are investigated with a range of peak irradiation from 25 to 45 kW/m^2, while the time to peak ranges from 280 to 480 s. For these pulses, the time to ignition measurements range from 300 to 483 s. The model can predict the in-depth temperature profiles with an average error lower than 9%. Model and experiments are then combined to study the validity of the solid-phase criteria for flaming ignition found in the literature, namely critical temperature, critical mass loss rate, critical energy and critical time-energy squared. We find that of these criteria, the best predictions are provided by the critical mass loss rate followed by the critical temperature, and the worst is the critical energy. Further analysis reveals the novel concept of simultaneous threshold values. While the mass loss rate is below 3 g/m^2 and the surface temperature is below 305 °C, ignition does not occur. Therefore these threshold values when exceeded simultaneously establish the earliest time possible for ignition.

1. Introduction

Fire is a complex phenomenon that encompasses a series of chemical and physical processes [1]. Before the combustible material can undergo combustion and release heat, it has to undergo ignition, which is a critical process that determines the initial growth of the fire [2]. Ignition is the onset of combustion, and flaming ignition the process by which the fast, exothermic, homogenous reaction is started, which then spreads further in the material, causing mass burning [3].

However, before flaming can occur, the solid fuel has to become gaseous [2–4]. The process through which the solid undergoes chemical decomposition and simultaneously transforms into gaseous fuel is called pyrolysis [3,4]. Because the molecules of solid hydrocarbon fuels like synthetic polymers or wood are large, they cannot be oxidized directly. Therefore, when exposed to heat, these molecules irreversibly decompose into smaller hydrocarbon chains which emerge as pyrolyzate gas [5]. Under the right conditions, these can ignite above the surface of the solid. Pyrolysis is the key process in the burning of solid fuels, because the rate at which a material transforms

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Nomenclature

Symbol	**Description**
A	pre-exponential factor
C	proportionality factor between time and energy-squared
c_p	heat capacity
E	activation energy
ΔH	heat of reaction
h_c	convective heat transfer coefficient
k	thermal conductivity
L	depth of the sample
$\dot{m}''$	mass flux per unit area
m''	mass per unit area
Q	energy
$\dot{q}''$	heat flux
$\dot{Q}'''$	heat generation per unit volume
R	universal gas constant
T	temperature
t	time
Y	mass fraction
z	depth into the sample

Greek letters

Symbol	**Description**
ε	emissivity
κ	radiative absorption coefficient
$\dot{\omega}'''$	reaction rate per unit volume
ρ	density
σ	Stefan–Boltzmann constant

Subscripts

Symbol	**Description**
0	initial
Al	aluminium
e	external
d	destruction
g	gas
i	condensed-phase species index
ig	at ignition
p	at peak
r	in-depth radiation
s	solid

into a gas phase fuel governs the timing of ignition and the energy release rate in the subsequent flames [4].

Most ignition studies consider constant irradiation representing the radiant irradiation from the heat source [3]. The exception to the ignition studies is the work by Reszka et al. [6] which considers a linearly increasing irradiation on a series of fuel types, and the work by Belcher et al. [7] which uses parabolic heat pulses. While using a constant irradiation is convenient due to its simplicity, this scenario is not realistic. Moreover, transient irradiation is a more comprehensive case for the understanding of pyrolysis where nonlinear heat transfer effects challenge the validity of solid-phase criteria for flaming ignition developed previously. We propose here that transient irradiation is the general problem to solid fuel ignition of which constant irradiation is a particular solution. It is essential to understand how and when ignition is reached with both constant and transient irradiation. This paper aims to carry out that study by combining numerical and experimental work. A parabolic pulse is chosen here because it is the simplest curve including both growth and decay.

The investigation of the ignition is done by comparing complementary experimental and computational works that use transient irradiation to investigate the pyrolysis of poly(methyl methacrylate) (PMMA), a polymer widely studied in fire science. The experiments measured the temperature profiles in PMMA samples heated by different irradiation pulses, thus providing validation for the numerical model.

This paper begins by summarizing the theoretical background on the classical ignition theory and four different ignition criteria found in the literature: critical energy, critical temperature, critical mass flux and time-energy squared. Afterwards, the experimental work is presented. The computational work, performed in a 1D pyrolysis model, GPyro [8], is then presented and validated using benchmark experiments by Kashiwagi et al. [9]. The results of the simulations are then compared to the transient irradiation experiments. Finally, the ignition criteria are assessed with respect to both constant and transient irradiation.

2. Classical ignition

Pyrolysis occurs inside the solid phase, and produces the gases necessary to feed the flame. In order to study flame ignition with a focus on solid-phase phenomena, there is need to replace the gas phase and invoke an ignition criterion. This criterion describes when ignition of the gas phase would take place by referring to conditions in the solid phase alone. In the literature, there are four criteria for piloted ignition. All four are empirical but based on combustion theories of different degrees of development. These are the critical energy, critical temperature, critical mass flux and time-energy squared.

For a thermally thick solid, the critical temperature criterion leads to Eq. (1) to establish the time to ignition calculated from the assumption of a critical surface temperature and a constant irradiation [4]. It is the most commonly used ignition criterion. It takes into account two main parameters, namely the ignition temperature and the thermal inertia of the fuel. However, this approach has several limitations. The greatest limitation is the difficulty of measuring the critical temperature [5], and its variation with regards to external heat flux and environmental conditions such as oxygen concentration. Therefore, the critical temperature criterion cannot give a certain value applicable for each fuel, but it varies with conditions under which it was determined [4,10].

$$\frac{1}{\sqrt{t_{ig}}} = \frac{2}{\sqrt{\pi}\sqrt{k\rho c}} \frac{\dot{q}_e''}{T_{ig} - T_0} \tag{1}$$

The critical mass loss rate is considered the most fundamental criterion. It assumes that ignition takes place when a critical flow of pyrolyzate mixes with air such that the mixture surpasses the lower flammability limit at the location of the pilot [3]. However, the experimental measurements are quite difficult, because the mass loss rate before ignition is very low [5]. Rich et al. [11] have proposed a theoretical model that relates the critical mass flux necessary for ignition to fuel properties using Spalding's number [12] and to environmental characteristics [11].

The critical energy criterion states that a sample will ignite after absorbing a certain amount of energy. The energy criterion relies on a series of simplifications, such as negligible heat losses and a constant ignition temperature [5]. Therefore, the criterion provides ranges of critical energy rather than a single value for each material.

$$Q_{ig} = \int_0^{t_{ig}} \dot{q}_e'' dt \tag{2}$$

The only criterion in the literature developed for transient irradiation is the time-energy squared correlation. This has been developed by Reszka et al. [6] and calculates the time to ignition by finding the squared integral of the incident irradiation up to the elapsed time. This method is applicable for incident irradiation fluxes that grow linearly. The methodology for this criterion relies on the linear dependency between $t_{ig}^{-\frac{1}{2}}$ and $\dot{q}_{ext}''$ and results in Eq. (3), where C represents