Combustion and Flame 161 (2014) 1752–1755

Contents lists available at ScienceDirect

Combustion and Flame

journal homepage: www.elsevier.com/locate/combustflame

Explosion criteria for a three-step Gray and Yang, non-isothermal branching reaction scheme in fluids with natural convection

Filipa Gonçalves de Azevedo [a], John F. Griffiths [b], Silvana S.S. Cardoso [a,*]

[a] Department of Chemical Engineering and Biotechnology, University of Cambridge, Pembroke St., Cambridge CB2 3RA, UK
[b] School of Chemistry, University of Leeds, Leeds LS2 9JT, UK

ARTICLE INFO

Article history:
Received 1 August 2013
Received in revised form 16 December 2013
Accepted 30 December 2013
Available online 24 January 2014

Keywords:
Natural convection
Explosion criteria
Gray and Yang
Low temperature combustion

ABSTRACT

Explosions may occur owing to thermal and branching effects in combustion processes. The ignition limits of a system are affected by the presence of natural convection, which develops inevitably in terrestrial systems. This work investigates the explosion criterion, through parametric sensitivity, for systems with a Gray and Yang, three-step, non-isothermal branching reaction scheme with natural convection. Ignition is identified with the maximum sensitivity of the non-dimensional temperature rise (T'_{max}) to the ratio of branching and termination reaction rates (τ_b/τ_t). The effects of self-heating, branching and natural convection on the time to ignition are analysed. A value of dimensionless temperature rise $T' = 5$ is found to be an appropriate explosion criterion for this system.

1. Introduction

Combustion occurs when a chemical reaction takes place under conditions of progressive self-acceleration owing to heat accumulation (thermal combustion) or when heat release is combined with the accumulation of active intermediate species through chain branching (chain-thermal or thermokinetic combustion). When the rate of heat generation in such a system overcomes the rate of heat loss or when the generation of active intermediates prevails over their consumption then the system becomes unstable and an explosion occurs. Throughout the years, several explosion criteria and approximations for the time to ignition have been used. On the one hand, thermal ignition is defined by the breakdown of quasi-stationary thermal stability of a system [1]. On the other hand, in chain theory, explosion is usually defined as a chemical runaway, in which the branching reaction rate exceeds the termination rate and thus the active intermediate concentration eventually becomes infinite [2,3].

Based on a skeleton kinetic scheme including both chain branching and heat release under spatially uniform conditions, as set out in the next section as Eqs. (1)–(3), by solving the eigenvalue equation in two dimensions Gray [4] showed that the individual, classical thermal and isothermal chain branching criteria for criticality were each supercritical with respect to that for a branching chain-thermal interaction. Our previous numerical simulations [5, Fig. 6] show that this conclusion remains valid in the presence of weak convection. That is, the surface separating the regions of the parameter space $\tau_H/\tau_D - \tau_b/\tau_t - Ra$ where explosive and non-explosive behaviours are observed, is continuous as the Rayleigh number tends to zero.

Some authors [6,7] define the "ignition delay" or "time to ignition" as the time needed for the temperature of the system to rise to infinity in homogeneous, adiabatic systems without reactant consumption while others define thermal runaway for first-order reaction systems with reactant consumption as the point when the dimensionless temperature rise $T' = 2$ [8,9] or $T' = 5$ [10,11]. Furthermore, Boddington et al. [12] suggested that ignition occurs when the peak temperature excess in a homogenous system with reactant consumption is most sensitive to its initial conditions. In order to avoid empirical approaches, Gray and Sherrington invoked Liapounov stability criteria to determine sufficient conditions for the stability, or otherwise, of a time dependent solution of the conservation equations [13,14]. However, the effect of the combination of both chain branching and natural convection on either explosion limits or the time to explosion in non-adiabatic systems is not amenable to this more rigorous approach but can be analysed through numerical analysis. We believe that the present investigation is the first to assess how these contributions affect explosive criteria in combustion systems.

2. Theoretical analysis

A three-step, unified Gray and Yang [15,16] reaction is considered for a gaseous system in a closed spherical vessel with radius

* Corresponding author.
E-mail addresses: mfcsg2@cam.ac.uk (F. Gonçalves de Azevedo), j.f.griffiths@leeds.ac.uk (J.F. Griffiths), sssc1@cam.ac.uk (S.S.S. Cardoso).

0010-2180/$ - see front matter © 2014 The Combustion Institute. Published by Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.combustflame.2013.12.026

Nomenclature

Roman symbols

a	concentration of species A
a_s	characteristic concentration of species A
C_p	specific heat at constant pressure
C_v	specific heat at constant volume
D_A	diffusion coefficient of species A
E	reaction activation energy
g	gravitational acceleration
$\mathbf{g}$	gravitational acceleration vector, $\mathbf{g} = [0; -g]$
k	reaction rate constant
L	characteristic length (radius) of the reactor
Le	Lewis number, $Le = \kappa/D_A$
n	reaction order
p	pressure
q	reaction exothermicity
Ra	Rayleigh number, $Ra = \beta g \Delta T_s L^3/(\nu\kappa)$
T	temperature
t	time
T'	dimensionless temperature, $T' = (T - T_0)/\Delta T_s$
t_s	characteristic time
$\mathbf{u}$	velocity vector
U	characteristic velocity
$\mathbf{x}$	spatial coordinates
Z	pre-exponential Arrhenius factor

Greek symbols

β	thermal expansion coefficient
ΔT_s	characteristic temperature increase
κ	thermal diffusivity
ν	kinematic viscosity
ρ	density
ρ_0	density at $T = T_0$
τ_b	timescale for branching at $T = T_0$
τ_D	timescale for diffusion
τ_H	timescale for exothermic reaction to heat the fluid by ΔT_s
τ_t	timescale for termination at $T = T_0$

Subscripts

0	initial conditions
b	branching conditions of Gray and Yang's reaction
i	initiation conditions of Gray and Yang's reaction
s	characteristic conditions
t	termination conditions of Gray and Yang's reaction

L and the model approach proposed by [5] is used. This mechanism considers initiation, branching and termination steps with a reactant species P and one intermediate active species A:

$$P \xrightarrow{k_i} A + \cdots \tag{1}$$

$$A + \cdots \xrightarrow{k_b} 2A \tag{2}$$

$$A + \cdots \xrightarrow{k_t} B. \tag{3}$$

The exothermicities and activation energies have been chosen as $q_i = 0,\ E_i = 0,\ q_b > 0,\ E_b > 0,\ q_t = 0,\ E_t > 0$ and $E_t/E_b > 1$. Both branching and termination steps are first-order reactions. A pool chemical approximation regarding the species P is taken into account, which is an acceptable approximation if its concentration is much larger than all of the other species or if its decay is very slow compared to the other reactions.

The fundamental equations describing the dynamics of the system are conservation of chemical species A, thermal energy, momentum and volume:

$$\frac{\partial a}{\partial t} + \mathbf{u}\cdot\nabla a = D_A\nabla^2 a + k_i + (k_b - k_t)a, \tag{4}$$

$$\frac{C_v}{C_p}\frac{\partial T}{\partial t} + \mathbf{u}\cdot\nabla T = \kappa\nabla^2 T + \frac{q_b k_b + q_t k_t}{\rho_0 C_p}a, \tag{5}$$

$$\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u}\cdot\nabla\mathbf{u} = -\frac{1}{\rho_0}\nabla(p - p_0) + \nu\nabla^2\mathbf{u} + \frac{\rho - \rho_0}{\rho_0}\mathbf{g}, \tag{6}$$

$$\nabla\cdot\mathbf{u} = 0. \tag{7}$$

The fluid is assumed to be incompressible and its density is taken as constant in all terms except in the buoyancy term in the momentum equation (Boussinesq approximation). The density of the fluid is assumed to vary linearly with temperature as $\rho = \rho_0[1 - \beta(T - T_0)]$, which is valid for $\Delta T/T_0 \ll 1$.

3. Numerical method

The four governing Eqs. (4)–(7) were solved numerically for initially pure P in a spherical batch reactor, using the finite-element solver Fastflo [17]. The algorithm used has been described previously [11,5,18,19]. The method of Picard of successive approximations was employed for linearisation, combined with a backward Euler time-stepping scheme, and the momentum and continuity equations were coupled using the Augmented-Lagrangian method [17]. Owing to the axisymmetric geometry, a semi-circular mesh of about 4000 elements was applied and a timestep of 0.01 s was used. As boundary conditions, at the wall, the temperature was kept at T_0 and both fluid velocity and flux of chemical species were set as zero. For convergence purposes, the relative velocity change between consecutive iterations, summed over all mesh nodes, was kept under 0.05 and continuity, Eq. (7), was satisfied within 1×10^{-5} s^{-1}.

4. Results and discussion

Simulations were made for a set of typical conditions taken from [5], as follows: $L = 6.4$ cm, $T_0 = 500$ K, $\rho_0 = 8.2$ mol m^{-3} (corresponding to a pressure of 34 kPa in a gaseous system at 500 K), $C_v = 190$ J mol^{-1} K^{-1}, $C_p = 229$ J mol^{-1} K^{-1}, $\kappa = \nu = D_A = 6.0 \times 10^{-4}$ m^2 s^{-1} ($Pr = Le = 1$), $q_b = 100$ kJ mol^{-1}, $E_b = 45$ kJ mol^{-1}, $E_t = 50$ kJ mol^{-1} and $Z_b = 28,700$ s^{-1}. The exothermicities of the termination and initiation step were set as zero. Under these conditions, this system can be described by three non-dimensional groups: $\tau_b/\tau_t = k_t/k_b$, $\tau_H/\tau_D = \rho_0 C_p \Delta T_s \kappa/(a_s q_b k_{b_0} L^2)$ and $Ra = \beta g \Delta T_s L^3/(\nu\kappa)$. To vary each of these groups, for each simulation, the values of Z_t, k_i and g were varied, whilst the remaining parameters were kept constant. The simulations were carried out for values of Ra between 0 and 10^5, *i.e.* for laminar flow.

In the problem studied here, heat is generated in the branching process, raising the temperature in the reactor. Since $E_t/E_b > 1$, the termination rate eventually overtakes the branching rate of A, as the temperature increases. This means that the active intermediate growth is always bounded [16], and therefore the chain explosion criterion (*i.e.* chemical runaway) is never met: the explosion, if present, is always thermal in origin. A common definition for this type of explosion is based on thermal runaway which is used for both thermal and chain-thermal combustion. Since the eventual domination of the (thermoneutral) termination hampers the heat