ORIGINAL PAPER

# Thermal explosion characteristics in a reduced kinetics model

**Suraju Olusegun Ajadi**

**Abstract**    The problem of thermal explosion arising from a spatially homogeneous reduced five steps reaction kinetic model, which comprises of the chain initiation, chain propagation/branching and chain termination steps is considered. By assuming realistic approximations, the pertubation technique was used to obtain expressions for thermal ignition time for the adiabatic system. In the non-adiabatic system, expressions for the critical heat loss parameter and the ignition temperature in the line of Semenov theory have been obtained. Analysis of the system involving some parameters, and the contributions of the heat released due to the termination reactions on the behaviour of the ignition times and Semenov parameters have been carried out and expressed graphically. Apart from confirming known results in literature, the results shed more light on hitherto unknown behaviour.

## Nomenclature

$C_P$    Specific heat capacity at constant pressure (JKg$^{-1}$K$^{-1}$)
$D_i$    Diffusion coefficients for species (m$^2$s$^{-1}$)
$E_i$    Activation energy for i reaction, $i = 0, 1, 2, 3, 4$ (Jmol$^{-1}$)
$F$    Fuel (Kgmol$^{-1}$)
$K$    Thermal conductivity (Wm$^{-1}$K$^{-1}$)
$M$    Inert body (Kgmol$^{-1}$)
$P_j$    Reaction products, $j = 1, 2$, (Kgmol$^{-1}$)

S. O. Ajadi (✉)
Department of Mathematics, Obafemi Awolowo University, Ile Ife 220005, Nigeria
e-mail: soajadi@yahoo.co.uk; sajadi@bgu.ac.il

| $Q$ | Overall heat released (J) |
|---|---|
| $Q_i$ | Exothermicity (heat evolved) in the $i$ reactions (J) |
| $Q_+$ | Heat released due to reaction in the non-adiabatic system (J) |
| $Q_-$ | Heat loss to the environment in the non-adiabatic system (J) |
| $q_i$ | $= \frac{Q_i}{Q}$, ratio of heat in $i$ reactions to the overall |
| $R$ | Universal gas constant ($JK^{-1}mol^{-1}$) |
| $R_j$ | Radicals, $j = 1, 2$, ($Kgmol^{-1}$) |
| $r$ | $= E_2/E_1$, ratio of activation energy of reactions II to I |
| $S$ | Surface area ($m^2$) |
| $T, T_0$ | Temperature, initial temperature (K) |
| $t$ | Time ($s$) |
| $v$ | Velocity ($ms^{-1}$) |
| $V$ | Volume ($m^3$) |
| $W_Y$ | Global reaction rate ($mol^{-1}s^{-1}m^{-3}$) |
| $w_i$ | Local reaction rate for $i$ reaction ($mol^{-1}s^{-1}m^{-3}$) |
| $Y$ | Molar concentration of species or reactant ($Kgmol^{-1}$) |

**Greek letters**

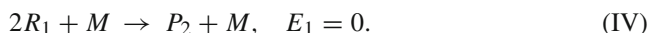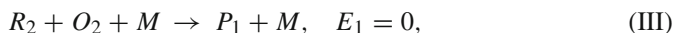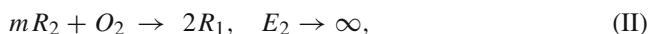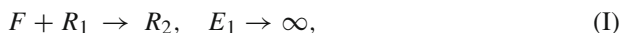| $\alpha$ | Reduced ambient temperature |
|---|---|
| $\beta_1, \beta_2$ | $= \frac{QY_{R_{10}}}{(C_P T_0)}, \frac{QM_{R_2}Y_{R_{20}}}{(C_P T_0 M_F)}$ |
| $\delta_i$ | Dimensionless parameter |
| $\theta, \theta_I, \theta_E$ | $= \frac{T-T_0}{\epsilon T_0}$ dimensionless, ignition, extinction temperatures |
| $\lambda_i$ | Pre-exponential factor for $i$ reaction ($s^{-1}$) |
| $\tau, \tau_{cr}$ | Dimensionless time, ignition time |
| $\rho$ | Density ($Kgm^{-3}$) |
| $\Psi$ | Semenov parameter |
| $\chi$ | Heat transfer coefficient (J/s) |

## 1 Introduction

The need for model with more detailed chemistry to represent the combustion of reactants(e.g hydrocarbon) has never been greater than it is today, as combustion scientists and engineers exploit computational method for the design and prediction of performance of practical combustion systems especially with regard to economical operation and minimisation of environmental pollution. Although the one-step model has served combustion theory well, particularly in the context of activation energy asymptotics, the neglect of radical or intermediary specie has precluded the modeling of many important phenomena. Thus, in recent years, there has been growing interest within the mathematical combustion community in the study of reduced mechanism. The majority of works dealing with such problems in combustion have been in the areas of spatially distributed system [1–12] and the spatially homogeneous problems [1,13–21].

The need for intensive studies along the line of reduced chemistry for a spatially homogeneous system containing an intermediate specie for two or more reactions steps are well documented in literature [1,13,21–23]. In the late 1960s, [16] developed the first reduced kinetic model for the oxidation of hydrocarbon fuels that qualitatively described many features observed experimentally. The mathematical model proved reliable for predictions of the oxidation characteristics, explosion limits, oscillations, and the results also validated experimental observations. As a further development, [17], extended [16] to a system with two reactive intermediate species by including a high energy autocatalytic reaction aim at promoting chain branching. Recently, [20] showed that [17] is defective as an extension of [16] because it does not simulate closed-vessel experiments. In a similar trend, development in the kinetic modeling for hydrogen oxidation has received remarkable attentions. For instance, using a two-step reaction model containing an intermediate specie, [14] considered the asymptotic analysis of a spatially homogeneous model of a non-isothermal branched-chain reaction leading to explosion time. Furthermore, [19] extended [14] to a four-steps to include two additional termination steps leading to fresh determination of criticality of certain parameters and explosion time.

Motivated by the above, we examine a spatially homogeneous two-radical reactions mechanism that accommodates initiation, branching, propagation and termination steps. Thus, the proposed model mechanism, which is an oxidation of reactant($F$) with two intermidates species is given by

$$F \rightarrow R_1, \quad E_0 \rightarrow \infty, \tag{O}$$

$$F + R_1 \rightarrow R_2, \quad E_1 \rightarrow \infty, \tag{I}$$

$$mR_2 + O_2 \rightarrow 2R_1, \quad E_2 \rightarrow \infty, \tag{II}$$

$$R_2 + O_2 + M \rightarrow P_1 + M, \quad E_1 = 0, \tag{III}$$

$$2R_1 + M \rightarrow P_2 + M, \quad E_1 = 0. \tag{IV}$$

Here $R_1$, $R_2$ stand for radicals, $F$ is the fuel, $M$ is the inert third body, $P_1$, $P_2$ are the reactions products, $O_2$ is the oxygen molecule. Equation (I) describes the process of fuel consumption, (II) represents branching or propagation depending on the value of $m$. In particular, if $m = 1$, (II) is a chain branching step and $m = 2$, is a chain propagation step. Reactions (III)–(IV) are regarded to as the radical consumption steps. Thus, the radical $R_1$ and $R_2$ are being converted to stable products. The initiation step (O) are often neglected, since it only initiates the reactions [20]. Note that in this scheme, as in many reduced schemes, the chemical 'reactions' do not represent specific steps in the oxidation mechanism. However, for $m = 1$ it may be associated with the hydrogen combustion [24] (page 410) or adapted for the methane combustions [6].

## 2 Problem formulation

The proposed model reactions mechanism is described by the usual variable $T$ denoting the temperature of the mixture, $Y_F$, representing the mass fraction for reactant(fuel), while $Y_{R_1}$, $Y_{R_2}$ representing the mass fraction of the radical 1 and radical 2

respectively. The mass and conservation equations for fuel, the intermediate species $(Y_F, Y_{R_1}, Y_{R_2})$ and the temperature $(T)$ for the kinetic model $(O-IV)$ are [20]

$$\frac{d\rho}{dt} = 0, \tag{2.0}$$

$$\frac{dY_F}{dt} = \frac{M_F}{\rho} W_F, \tag{2.1}$$

$$\frac{dY_{R_1}}{dt} = \frac{M_{R_1}}{\rho} W_{R_1}, \tag{2.2}$$

$$\frac{dY_{R_2}}{dt} = \frac{M_{R_2}}{\rho} W_{R_2}, \tag{2.3}$$

$$\frac{dT}{dt} = \frac{1}{\rho C_P} \sum_{i=1}^{4} Q_i w_i - \frac{\chi S}{\rho C_p V} (T - T_0), \tag{2.4}$$

where $\rho$ is the constant density, $C_P$ is the specific heat capacity at constant pressure, $Q_i (i = 1, 2, 3, 4)$ are the quantities of heat released by each step and $M_F$, $M_{R_1}$, $M_{R_2}$ are the molecular weights of fuel, radicals 1 and 2 respectively, while $E_1$ and $E_2$ are the activation energies for the branching (or propagation) step. The global reaction rates $W_F$, $W_{R_1}$, $W_{R_2}$ and the local reaction rates, $w_1$, $w_2$, $w_3$ and $w_4$ for Eqs. (2.1)–(2.4) are defined as follows;

$$
\begin{aligned}
W_F &= -w_1, \\
W_{R_1} &= -w_1 + 2w_2 - 2w_4, \\
W_{R_2} &= w_1 - mw_2 - w_3,
\end{aligned}
\tag{2.5}
$$

where

$$
\begin{aligned}
w_1 &= \lambda_1 \rho^2 (Y_F/M_F)(Y_{R_1}/M_{R_1}) \exp(-E_1/RT), \\
w_2 &= \lambda_2 \rho^{m+1} (Y_{R_2}/M_{R_2})^m (Y_{O_2}/M_{O_2}) \exp(-E_2/RT), \\
w_3 &= \lambda_3 \rho^3 (1/M)(Y_{R_2}/M_{R_2})(Y_{O_2}/M_{O_2}), \\
w_4 &= \lambda_4 \rho^3 (Y_{R_1}/M_{R_1})^2 (1/M).
\end{aligned}
\tag{2.6}
$$

The Eqs. (2.0)–(2.4) are the governing equations for the model under consideration, where (2.0) is the continuity equation, (2.1)–(2.3) are the species equations and (2.4) is the energy (or tempearture) equation. The momentum balance of the separate species will not be written down since they play no role in the sequel and no momentum is created by the chemical reactions [25].

## 3 Dimensionless homogeneous reaction system

The dimensional analysis has served as conceptual tool to understand physical situations involving certain physical quantities and also used to form reasonable hypotheses

about complex physical situations that can be tested by experiment or by more developed theories of the phenomena described by relations such as

$$dY_F/dt = M_F/\rho W_F,$$
$$dY_{R_1}/dt = M_{R_1}/\rho W_{R_1},$$
$$dY_{R_2}/dt = M_{R_2}/\rho W_{R_2},$$
$$dT/dt = 1/(\rho C_P) \sum_{i=1}^{4} Q_i W_i - \frac{\chi S}{\rho C_p V}(T - T_0). \tag{3.1}$$

In explicit forms, (3.1) becomes

$$dY_F/dt = -M_F/\rho[\lambda_1\rho^2(Y_F/M_F)(Y_{R_1}/M_{R_1})\exp(-E_1/RT)],$$
$$dY_{R_1}/dt = M_{R_1}/\rho[-\lambda_1\rho^2(Y_F/M_F)(Y_{R_1}/M_{R_1})\exp(-E_1/(RT))$$
$$+2\lambda_2\rho^{m+1}(Y_{R_2}/M_{R_2})^m(Y_{O_2}/M_{O_2})\exp(-E_2/(RT))]$$
$$+M_{R_1}/\rho[-2\lambda_4\rho^3(1/M)(Y_{R_1}/M_{R_1})^2],$$
$$dY_{R_2}/dt = M_{R_2}/\rho[\lambda_1\rho^2(Y_F/M_F)(Y_{R_1}/M_{R_1})\exp(-E_1/(RT))$$
$$-m\lambda_2\rho^{m+1}(Y_{R_2}/M_{R_2})^m(Y_{O_2}/M_{O_2})\exp(-E_2/(RT))]$$
$$+M_{R_2}/\rho[-\lambda_3\rho^3(1/M)(Y_{R_2}/M_{R_2})(Y_{O_2}/M_{O_2})],$$
$$dT/dt = 1/(\rho C_P)[Q_1\lambda_1\rho^2(Y_F/M_F)(Y_{R_1}/M_{R_1})\exp(-E_1/(RT))$$
$$+Q_2\lambda_2\rho^{m+1}(Y_{R_2}/M_{R_2})^m(Y_{O_2}/M_{O_2})\exp(-E_2/(RT))]$$
$$+M_{R_1}/(\rho C_P)[Q_3\lambda_3\rho^3(1/M)(Y_{R_2}/M_{R_2})(Y_{O_2}/M_{O_2})$$
$$+Q_4\lambda_4\rho^3(Y_{R_1}/M_{R_1})^2(1/M)] - \frac{\chi S}{\rho C_p V}(T - T_0), \tag{3.2}$$

where the initial conditions are

$$Y_F(0) = Y_{F0}, \ Y_{R_1}(0) = Y_{R10}, \ Y_{R_2}(0) = Y_{R20}, \text{ and } T(0) = T_0. \tag{3.3}$$

We may non-dimensionalize (3.2)–(3.3) using the following,

$$\theta = (T - T_0)/(\alpha T_0), \quad Y_F = (C_P T_0 M_F)/(Q M_{R_1})X,$$
$$Y_{R_1} = C_P T_0/QY, \quad Y_{R_2} = (C_P T_0 M_F)/(Q M_{R_2})Z,$$
$$t = (M_F \exp(1/\alpha)/(\rho Y_{F_0}\lambda_1)\tau, \quad r = E_2/E_1 \text{ and } \alpha = RT_0/E_1. \tag{3.4}$$

After substituting (3.4) into (3.2), we have

$$\frac{dX}{d\tau} = -\frac{1}{\delta_1}\exp\left(\frac{\theta}{1+\alpha\theta}\right)XY,$$
$$\frac{dY}{d\tau} = -\frac{1}{\delta_1}\exp\left(\frac{\theta}{1+\alpha\theta}\right)XY + \frac{2\delta_2}{\mu}\exp\left(\frac{r\theta}{1+\alpha\theta}\right)Z^m - 2\delta_4 Y^2,$$

$$\frac{dZ}{d\tau} = \frac{\mu}{\delta_1} \exp\left(\frac{\theta}{1+\alpha\theta}\right) XY - m\delta_2 \exp\left(\frac{r\theta}{1+\alpha\theta}\right) Z^m - \delta_3 Z,$$

$$\frac{d\theta}{d\tau} = \frac{q_1}{\alpha\delta_1} \exp\left(\frac{\theta}{1+\alpha\theta}\right) XY + \frac{q_2\delta_2}{\alpha\mu} \exp\left(\frac{r\theta}{1+\alpha\theta}\right) Z^m + \frac{q_3\delta_3}{\alpha\mu} Z + \frac{q_4\delta_4}{\alpha} Y^2$$

$$- \frac{q_1\delta_{10}}{\Psi\alpha\delta_1}\theta, \tag{3.5}$$

and the initial conditions

$$X(0) = \delta_1, \; Y(0) = \beta_1, \; Z(0) = \beta_2 \text{ and } \theta(0) = 0, \tag{3.6}$$

where

$$\delta_1 = (QM_{R_1}Y_{F0})/(C_P T_0 M_F), \; \delta_{10} = \frac{Q\delta_1}{\rho C_P T_0}, \; \frac{1}{\Psi} = \frac{SRT_0^2\chi}{C_{F0}\lambda_1 Q_1 VE_1} \exp\left(\frac{1}{\alpha}\right),$$

$$\delta_2 = \lambda_2/\lambda_1 Y_{O_2} M_F/(M_{O_2} Y_{F0}) \left((\rho C_P T_0 M_F)/(QM_{R_2}^2)\right)^{m-1} \exp(\frac{(1-r)}{\alpha}),$$

$$\delta_3 = \lambda_3/\lambda_1 (\rho Y_{0_2} M_F)/(MM_{O_2} Y_{F0}) \exp(1/\alpha), \quad \mu = M_{R_2}^2/(M_{R_1} M_F),$$

$$\delta_4 = \lambda_4/\lambda_1 (\rho C_P T_0 M \exp(1/\alpha))/(MQM_{R_1} Y_{F0}), \quad Q = \sum_{i=1}^{4} Q_i,$$

$$\beta_1 = \frac{Y_{R_{10}}Q}{C_P T_0}, \; \beta_2 = \frac{Y_{R_{20}}QM_{R_2}}{C_P T_0 M_F}, \; q_i = Q_i/Q, \quad i = \{2, 3, 4\}.$$

The analysis of the system is usually based on these governing equations resulting from the differential balance laws. The temporal evolution of a chemical reaction scheme is derived numerically from the simultaneous integration of a set of differential equations, each one representing the concentration of a specie in the system, and also the reactant temperature. However, prediction of most practical applications using these equations require detailed information of the physics of the problem. Thus, most analysis are based on simplifying mathematical approximations. For example, safe simplifications such as the adiabatic approximation, which corresponds to $\chi = 0$ or $\Psi = \infty$ and the isothermal approximation ($\chi = \infty$) are readily used. If we assume adiabatic approximation, where the heat production rate greatly exceeds the rate of heat loss to the surrounding, then the system of reactions can be approximated by the system of spatially homogeneous ordinary non-linear differential equations [19,20]

## 3.1 Method of solutions (adiabatic case)

The method of asymptotic analysis is a formal series expansion which has the property that truncating the series after a finite number of terms provides an approximation to a given function as the argument tend towards a particular, often infinite point. In many problems, we seek an asymptotic expansion as $\alpha \to 0$ of a function $u(\alpha, t)$, where $t$ is an independent variable. The asymptotic behaviour of the function with respect to

$\alpha$ may depend upon $t$, in which case we may say that the expansion is non-uniform. In keeping with [14] and [19], we take an appropriate expansion in the activation energy asymptotic limit($\alpha \to 0$) for $X$, $Y$, $Z$ and $\theta$ in the form

$$\theta = \theta_0 + \alpha\theta_1 + h.o.t,$$
$$X = \delta_1 + \alpha X_1 + h.o.t,$$
$$Y = \alpha^s Y_1 + h.o.t,$$
$$Z = \alpha^p Z_1 + h.o.t, \tag{3.7}$$

where $h.o.t$ refers to 'higher order terms' and $\alpha$ is a small parameter, where $s$ and $p$ are numerical exponents to be given specific values later. After the substitution of (3.7), (3.5) becomes

$$\frac{dX_1}{d\tau} = 0, \quad \Rightarrow \quad X_1 = 0, \tag{3.8}$$

$$\frac{dY_1}{d\tau} = \frac{-1}{\delta_1}(\delta_1 + X_1)Y_1\exp(\theta_0) + \frac{2\delta_2}{\mu}\alpha^{pm-s}Z_1^m\exp(r\theta_0) - 2\delta_4\alpha^s Y_1^2, \tag{3.9}$$

$$\frac{dZ_1}{d\tau} = \frac{\mu}{\delta_1}\alpha^{s-p}(\delta_1 + X_1)Y_1\exp(\theta_0) - m\delta_2\alpha^{p(m-1)}Z_1^m\exp(r\theta_0) - \delta_3 Z_1, \tag{3.10}$$

$$\frac{d\theta_0}{d\tau} + \alpha\frac{d\theta_1}{d\tau} = \frac{q_1}{\delta_1}(\delta_1 + \alpha X_1)Y_1\exp(\theta_0)\alpha^{s-1} + \frac{q_2}{\mu}\delta_2\alpha^{pm-1}Z_1^m\exp(r\theta_0)$$
$$+ \frac{q_3}{\mu}\delta_3\alpha^{p-1}Z_1 + q_4\delta_4\alpha^{2s-1}Y_1^2. \tag{3.11}$$

On inserting (3.7) into Eq. (3.6), we obtain

$$\theta_0(0) = 0, \quad X_1(0) = 0, \quad Y_1(0) = \beta_1 \quad \text{and} \quad Z_1(0) = \beta_2, \tag{3.12}$$

where $\beta_1$ and $\beta_2$ are very small numbers, which implies that at the onset of reaction, radical concentration is not absolutely zero [18]. Equation (3.9) may have confirm known approximation(the pool chemical approximation) or neglect of fuel in analysis due to negligible change [2,20]. We shall now collect like orders for the Eqs. (3.9)–(3.12) for different choices of $p$, $s$ and $m$.

3.2 Case I ($m = 1, q_1 \to 0$)

If we let $m = p = s = 1$, then (3.9)–(3.12) become

$$\frac{dY_1}{d\tau} = -Y_1\exp(\theta_0) + 2\frac{\delta_2}{\mu}\exp(r\theta_0)Z_1, \tag{3.28}$$

$$\frac{dZ_1}{d\tau} = \mu Y_1\exp(\theta_0) - \frac{\delta_2}{\mu}\exp(r\theta_0)Z_1 - \delta_3 Z_1, \tag{3.29}$$

$$\frac{d\theta_0}{d\tau} = q_1 Y_1 \exp(\theta_0) + \frac{q_2\delta_2}{\mu}\exp(r\theta_0)Z_1 + \frac{q_3\delta_3}{\mu}Z_1. \tag{3.30}$$

Suppose heat liberated by the propagation reaction($I$) is negligible($q_1 \to 0$) and that $\mu$ is very small that($\mu^2 \to 0$) [26], then (3.28) when divided by (3.30) gives

$$\frac{dZ_1}{d\theta_0} = \frac{-\mu(\delta_2\exp(r\theta_0)+\delta_3)}{q_2\delta_2\exp(r\theta_0)+q_3\delta_3}, \tag{3.31}$$

which on integration gives

$$Z_1 = \frac{\mu}{r}\ln\left[D_0\exp(-r/q_3\theta_0)\,(q_2\delta_2\exp(r\theta_0)+q_3\delta_3)^{\frac{1}{q_3}-\frac{1}{q_2}}\right], \tag{3.32}$$

where $D_0$ is a constant of integration. Using the initial condition $Z_1(0) = \beta_2$, (3.32) becomes

$$Z_1 = \frac{\mu}{r}\ln\left[\exp\left(\frac{r\beta_2}{\mu}\right)\exp(-r/q_3\theta_0)\left(\frac{q_2\delta_2\exp(r\theta_0)+q_3\delta_3}{q_2\delta_2+q_3\delta_3}\right)^{\frac{1}{q_3}-\frac{1}{q_2}}\right]. \tag{3.33}$$

On inserting (3.32) into (3.30), we obtain the expression

$$\tau = \int_0^\theta \frac{r\,ds}{(q_2\delta_2\exp(rs)+q_3\delta_3)\ln\left[\exp(r\beta_2/\mu)\exp(-r/q_3s)(P)^{\frac{1}{q_3}-\frac{1}{q_2}}\right]}, \tag{3.34}$$

where $P = \left(\frac{q_2\delta_2\exp(r\theta_0)+q_3\delta_3}{q_2\delta_2+q_3\delta_3}\right)$. The expression for ignition time ($\tau = \tau_{cr}$)

$$\tau_{cr} = \int_0^\infty \frac{r\,ds}{(q_2\delta_2\exp(rs)+q_3\delta_3)\ln\left[\exp(r\beta_2/\mu)\exp(-r/q_3s)(P)^{\frac{1}{q_3}-\frac{1}{q_2}}\right]}. \tag{3.35}$$

### 3.3 Case II ($m = 1, q_1, q_2 \to 0$)

In another consideration, it is established that branching steps ($II$), which are mostly endothermic competes with the termination steps ($III$ and $IV$), which are exothermic, it is sufficient to assume that the bulk of heat released to the system is supplied by $q_3$ and $q_4$ ([3] and [20] ). After assuming that $q_1, q_2 \to 0$, and dividing (3.28) by (3.30) we obtain

$$\frac{dZ_1}{d\theta_0} = \frac{-\mu(\delta_2\exp(r\theta_0)+2\delta_3)}{q_3\delta_3}, \tag{3.36}$$

which on integration gives

$$Z_1 = \frac{-\mu}{q_3\delta_3}\left(\frac{\delta_2}{r}\exp(r\theta_0) + \delta_3\theta_0\right) + \text{constant}.$$

Using the initial condition $Z_1(0) = \beta_2$, then

$$Z_1 = \frac{-\mu}{rq_3\delta_3}(1 - \exp(r\theta_0)) + \left(\beta_2 - \frac{\mu}{q_3}\theta\right). \tag{3.37}$$

When (3.37) is substituted into (3.30), we obtain

$$\frac{d\theta_0}{d\tau} = \frac{q_3\delta_3}{\mu}\left[\frac{\mu\delta_2}{rq_3\delta_3}(1 - \exp(r\theta_0)) + \beta_2 - \frac{\mu}{q_3}\theta_0\right],$$

and the time($\tau$) is expressed as

$$\tau = \frac{\mu}{q_3\delta_3}\int^{\theta_0}\frac{ds}{\left[\mu\delta_2/(rq_3\delta_3)(1 - \exp(rs)) + \beta_2 - \frac{\mu}{q_3}s\right]}. \tag{3.38}$$

The expression for the ignition time is

$$\tau_{cr} = \frac{\mu}{q_3\delta_3}\int_0^\infty\frac{d\theta_0}{\left[\mu\delta_2/(rq_3\delta_3)(1 - \exp(r\theta_0)) + \beta_2 - \mu/q_3\theta_0\right]}. \tag{3.39}$$

## 4 Non-adiabatic system

We consider a reactive exothermic system, which releases heat to the surrounding environment. In order to obtain analytical solution and in keeping with tradition, we assume the 'pool approximation' for the reactant, otherwise the changing reactant concentration has to be considered. Suppose we take guidance from experimental and numerical data in flame analysis, which shows that at least close to the flammability limit the radical level is very low, suggesting that the radicals are in steady state ([17], pg. 63 and [6], pg. 174). Then the system of Eqs. (3.5) reduce to

$$\frac{dY}{d\tau} = -\exp\left(\frac{\theta}{1 + \alpha\theta}\right)Y + \frac{2\delta_2}{\mu}\exp\left(\frac{r\theta}{1 + \alpha\theta}\right)Z - 2\delta_4 Y^2 = 0,$$

$$\frac{dZ}{d\tau} = \mu\exp\left(\frac{\theta}{1 + \alpha\theta}\right)Y - \delta_2\exp\left(\frac{r\theta}{1 + \alpha\theta}\right)Z - \delta_3 Z = 0,$$

$$\frac{\alpha}{q_1}\frac{d\theta}{d\tau} = \exp\left(\frac{\theta}{1 + \alpha\theta}\right)Y + \frac{q_2\delta_2}{q_1\mu}\exp\left(\frac{r\theta}{1 + \alpha\theta}\right)Z + \frac{q_3\delta_3}{q_1\mu}Z + \frac{q_4\delta_4}{q_1}Y^2 - \frac{\delta_{10}}{\delta_1\Psi}\theta. \tag{4.0}$$

After solving the first two equations of (4.0) simultaneously, the steady state solutions $S_i(Y_i, Z_i)$ are

$$S_1(0,0), \quad S_2(\beta_1, \beta_2) \quad \text{and} \quad S_3\left[\frac{1}{2\delta_4} S \exp\left(\frac{\theta}{1+\alpha\theta}\right), \frac{\mu}{2\delta_4} S \exp\left(\frac{2\theta}{1+\alpha\theta}\right)\right],$$

where $S = \left(\dfrac{\delta_2 \exp\left(\frac{r\theta}{1+\alpha\theta}\right) - \delta_3}{\delta_2 \exp\left(\frac{r\theta}{1+\alpha\theta}\right) + \delta_3}\right)$. The trivial steady state $S_1$ coincides with the one-step reaction(Semenov model), while the steady states $S_2$ and $S_3$ depict the chain-thermal ignition system.

4.1 Case I: $S_2$

After inserting the steady state $S_2$ into the energy Eq. (4.0), we have

$$\frac{\alpha}{q_1\beta_1}\frac{d\theta}{d\tau} = \exp\left(\frac{\theta}{1+\alpha\theta}\right) + q_{12}\exp\left(\frac{r\theta}{1+\alpha\theta}\right) + q_{34} - \frac{1}{\Psi}\theta, \qquad (4.1)$$

where for simplicity

$$q_{12} = \frac{q_2\delta_2}{q_1\beta_1\mu}, \quad q_{34} = \frac{q_3\delta_3\beta_2}{q_1\beta_1\mu} + \frac{q_4\delta_4\beta_1}{q_1}, \quad \text{and} \quad \frac{\delta_{10}}{\delta_1\beta_2} = 1$$

Let the steady state form of (4.1) for the existence of critical conditions be

$$\exp\left(\frac{\theta}{1+\alpha\theta}\right) + q_{12}\exp\left(\frac{r\theta}{1+\alpha\theta}\right) + q_{34} - \frac{1}{\Psi}\theta \equiv Q_+ - Q_-, \qquad (4.2)$$

where $Q_+$ and $Q_-$ refers to the rate of heat produced and the rate heat loss to the environment respectively. Applying the Semenov analysis on Eq. (4.2), the criterion for the onset of thermal ignition are identified by the relations [27]

$$Q_+ = Q_-, \qquad (4.3)$$

$$\frac{dQ_+}{d\theta} = \frac{dQ_-}{d\theta}. \qquad (4.4)$$

Thus,

$$\exp\left(\frac{\theta}{1+\alpha\theta}\right) + q_{12}\exp\left(\frac{r\theta}{1+\alpha\theta}\right) + q_{34} - \frac{1}{\Psi}\theta = 0, \qquad (4.5)$$

and

$$\exp\left(\frac{\theta}{1+\alpha\theta}\right) + rq_{12}\exp\left(\frac{r\theta}{1+\alpha\theta}\right) - \frac{1}{\Psi}(1+\alpha\theta)^2 = 0. \qquad (4.6)$$

For convenience, it is possible to take the first two terms of the quadratic form of the exponential function [15]

$$1 + \frac{n\theta}{1+\alpha\theta} + q_{12}\left[1 + \frac{nr\theta}{1+\alpha\theta}\right] + q_{34} - \frac{1}{\Psi}\theta = 0, \tag{4.7}$$

and

$$1 + \frac{n\theta}{1+\alpha\theta} + rq_{12}\left[1 + \frac{nr\theta}{1+\alpha\theta}\right] - \frac{1}{\Psi}(1+\alpha\theta)^2 = 0, \tag{4.8}$$

where $n$ is a constant($n \neq 1$). Solving (4.7) and (4.8) simultaneously,

$$A\theta^2 - B\theta + C = 0, \tag{4.9}$$

where

$$A = \left[n(1 + r^2 q_{12}) + \alpha(1 - 2n)(1 + rq_{12})\right], \ B = (1 - n)(1 + rq_{12}) - 3\alpha C,$$
$$\text{and} \ C = 1 + q_{12} + q_{34}.$$

After taking binomial expansion, the solution of (4.9) becomes

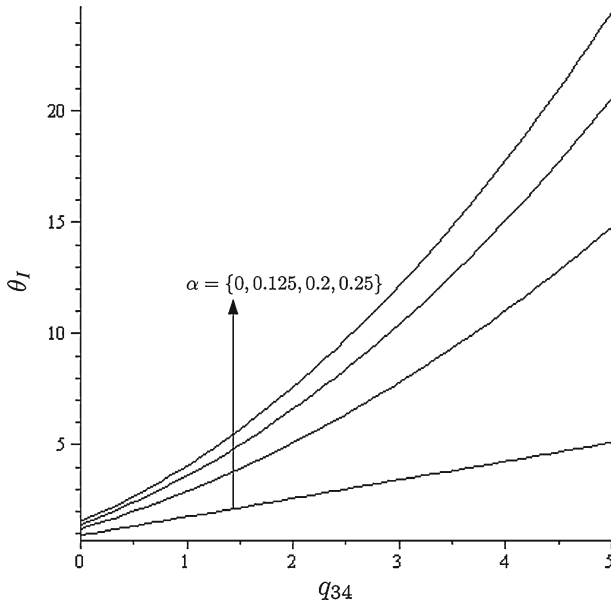$$\theta = \theta_I = \frac{C}{B} \ \text{or} \ \theta = \theta_E = \frac{B}{A} - \frac{C}{B}. \tag{4.10}$$



**Fig. 1** $\theta_I$ versus $q_{34}$, for some $\alpha$ and $q_{21} = 0.1$ for Eq. (3.35)

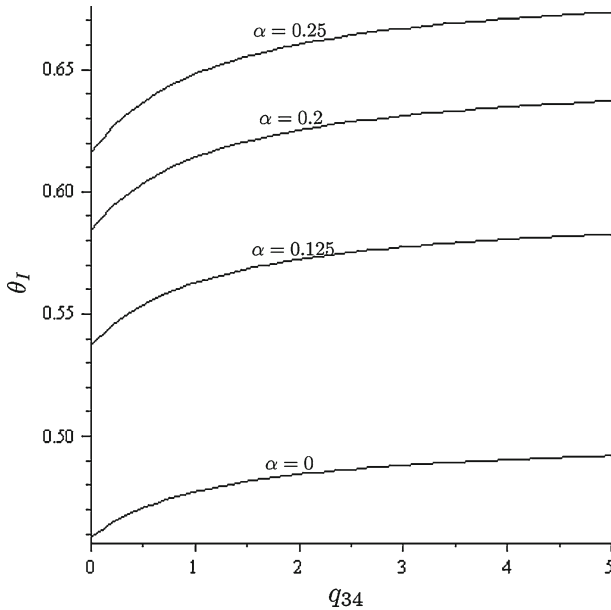**Fig. 2** $\theta_I$ versus $q_{34}$, for some $\alpha$ and $r = 2$ for Eq. (3.39)

Being the only realistic critical temperature, the asymptotic expansion of $\theta_I$ in $\alpha$ in (4.10),

$$\theta_I = \frac{1 + q_{12} + q_{34}}{(1-n)(1+rq_{12})} \left[ 1 + 3\alpha \left( \frac{1 + q_{12} + q_{34}}{(1-n)(1+rq_{12})} \right) \right]. \tag{4.11}$$

In the simplified case of $n = q_{12} = q_{34} = 0$, we obtain the well known results obtained by Semenov ($\theta_{cr} = 1$ and $\Psi = e^{-1}$). By substituting (4.11) into (4.5), the expression for the critical Semenov parameter thus becomes,

$$\frac{1}{\Psi_{cr}} = \frac{\exp\left(\frac{\theta_I}{1+\alpha\theta_I}\right) + q_{12}\exp\left(\frac{r\theta_I}{1+\alpha\theta_I}\right) + q_{34}}{\theta_I} \tag{4.12}$$

### 4.2 Case II: $S_3$

In this case, after a similar analysis, and assuming that for small $\delta_3(S = 1)$, the criterion for thermal criticality (4.3–4.4) leads to

$$(1 + q'_{34})\exp\left(\frac{2\theta}{1+\alpha\theta}\right) + q'_{12}\exp\left(\frac{(r+2)\theta}{1+\alpha\theta}\right) - \frac{1}{\Psi}\theta = 0, \tag{4.13}$$

and

$$2(1 + q'_{34}) \exp\left(\frac{2\theta}{1+\alpha\theta}\right) + rq'_{12} \exp\left(\frac{(r+2)\theta}{1+\alpha\theta}\right) - \frac{1}{\Psi}(1+\alpha\theta)^2 = 0, \quad (4.14)$$

where

$$q'_{12} = \frac{2q_2\delta_2}{q_1}, \quad q'_{34} = \frac{2q_3\delta_3}{q_1} + \frac{q_4}{2q_1}, \quad \text{and} \quad \frac{2\delta_{10}\delta_4}{\delta_1} = 1.$$

We combine (4.13) and (4.14) to get the quadratic equation

$$E\theta^2 - F\theta + G = 0, \quad (4.15)$$

where

$$E = \left[4n\alpha - 2\alpha - 4n)(1 + q'_{34}) + (2n\alpha r + 4\alpha n - r\alpha - 2\alpha - nr^2 - 2nr - 4n)\right],$$
$$F = (1 - n)\left[2(1 + q'_{34}) + (r+2)q'_{21}\right] - 3\alpha G, \quad \text{where} \quad G = 1 + q'_{12} + q'_{34}.$$

The critical or ignition temperature is

$$\theta_I = \frac{(1 + q'_{12} + q'_{34})/(1-n)}{\left[2(1 + q'_{34}) + (r+2)q'_{21}\right]} \left[1 + \frac{3\alpha(1 + q'_{12} + q'_{34})/(1-n)}{\left[2(1 + q'_{34}) + (r+2)q'_{21}\right]}\right], \quad (4.16)$$

while the expression for the critical Semenov parameter is

$$\frac{1}{\Psi_{cr}} = \frac{(1 + q'_{34}) \exp\left(\frac{2\theta_I}{1+\alpha\theta_I}\right) + q'_{12} \exp\left(\frac{(r+2)\theta_I}{1+\alpha\theta_I}\right)}{\theta_I}. \quad (4.17)$$

In practise [28], it is interesting to see how the steady state temperature ($\theta$) varies with the bifurcation parameter ($\Psi$) in Eqs. (4.12) and (4.17). The plot of $\Psi_{cr}$ against $\theta_I$ for Eqs. (4.11) and (4.17) are presented in Figs. 3 and 4 respectively.

## 5 Conclusion

The analysis of thermal explosion characteristics for a five-step kinetics model has been considered. The pertubation method technique has been used to solve the homogeneous adiabatic system, while the classical Semenov procedure has been exploited to obtain the critical temperature and parameter for thermal ignition. The influence of various parameters embedded in the system on the ignition time ($\tau_{cr}$), the ignition temperature ($\theta_I$) and the critical Semenov parameter ($\Psi_{cr}$) have been investigated.

In line with the physics of the problem, for the adiabatic case, Figs. 5 and 6 show that as the heat contribution ($q_3$) by the termination reaction step increases, the ignition time reduces for some activation energy ratios ($r$). By comparision, in the absence
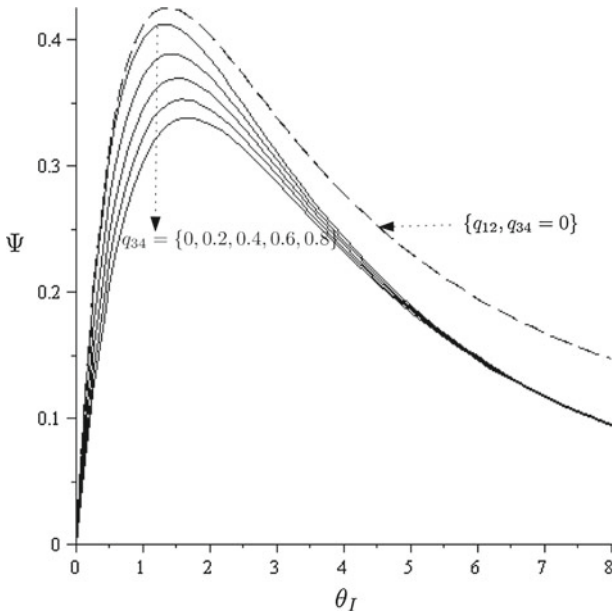
**Fig. 3** $\Psi_{cr}$ versus $\theta_I$ for some $q_{34}$, $q_2 = 0.1$ and $\alpha = 0.125$ for Eq. (4.12)
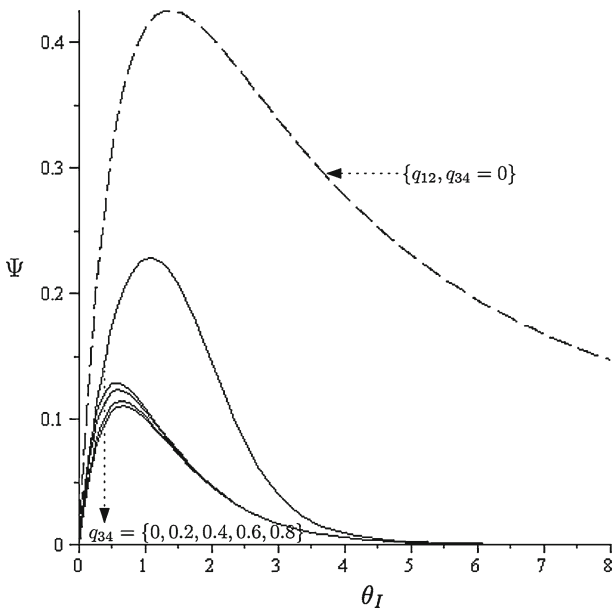


**Fig. 4** $\Psi_{cr}$ versus $\theta_I$ for some $q_{34}$, $q_2 = 0.1$ and $\alpha = 0.125$ for Eq. (4.17)
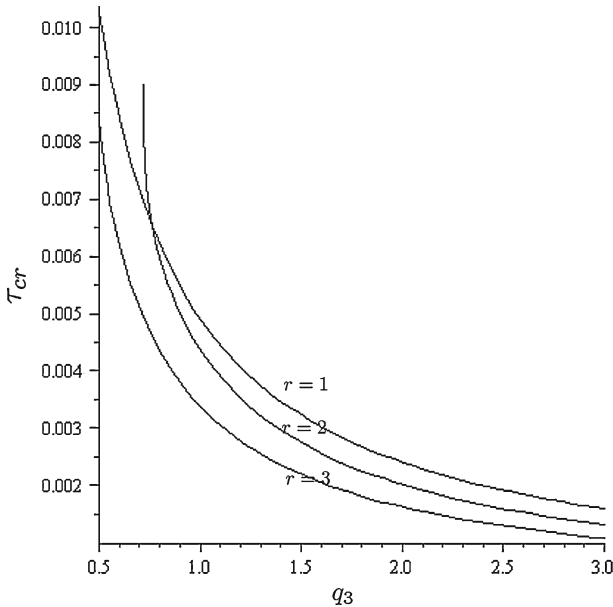
**Fig. 5** $\tau_{cr}$ versus $q_3$, for some $r$ and $q_2 = 0.1$ for Eq. (3.35)

of other non-exothermic energy inputs ($q_1, q_2 \rightarrow 0$), Fig. 6 shows that the ignition delay time is lower than (Fig. 5). Hence, endothermic reactions may serve as an inhibitor, which delays the occurrence of thermal ignition. In the non-adiabatic case, after exploiting the steady state approximation for the intermediate species, expressions for the ignition temperature and the critical heat loss parameter have been obtained. Figures 1 and 2 show the plots of the ignition temperature against the heat contribution due to the termination reaction steps ($q_{34}$). In line with expectation, it is observed that that the ignition temperature ($\theta_I$) increases with increasing adiabatic temperature parameter ($\alpha$). The variations of the bifurcation parameters ($\Psi$) with the steady state temperature ($\theta_I$) are shown in Figs. 3 and 4. In these figures, the curves conforms with established results [28], particularly the special case of $q_{12} = q_{34} = 0$ (broken curves). Furthermore, it is also evident that the maximum subcritical temperature rise lies in the neighbourhood of $\theta_I = 1$. It is observed that as the heat contribution from the exothermic heat source increases, the heat transfer parameter increases considerably. Inspite of this, thermal ignition is expected to occur when the rate of heat produced can no longer keep pace with that of heat loss. In addition, Fig. 4 shows that the temperature dependent steady state intermediate species concentration (case $II$) leads to a comparatively high heat transfer parameter as compared with the constant steady state intermediate species concentration in Fig. 3 (case $I$). This shows that a reactive system with highly exothermic reactions steps attains ignition or criticality faster with high heat transfer. Apart from validating known results, this study would be very useful in safety applications in the industry and opens more doors for future works.
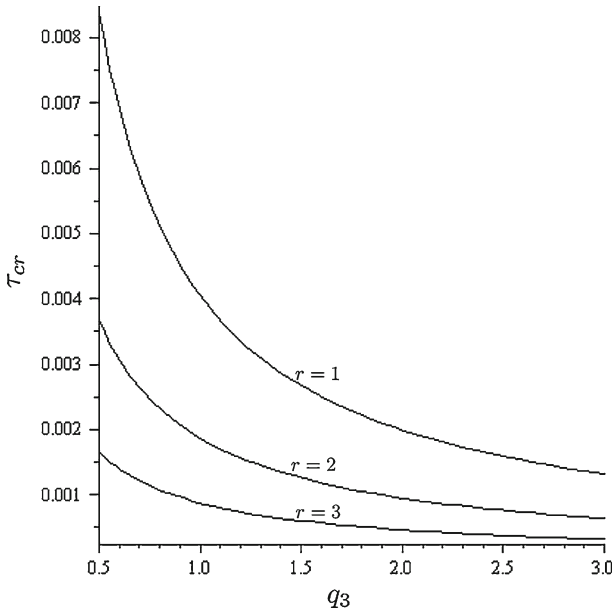
**Fig. 6** $\tau_{cr}$ versus $r$, for some $\beta_2$ and $q_2 = 0.2$ for Eq. (3.35)

## Appendix

In the present work, we use the available data from methane combustion experiment in literature [8,18,22,29] and [30, Appendix 1], the plot of $\tau_{cr}$ in (3.35) and (3.39) for some parameters embedded in the system are shown in Figs. 5–2.

$\lambda_i = 0.1\,\mathrm{s}^{-1}$, $E_1 = 1.1473E(5)\,\mathrm{Jmol}^{-1}$, $Q_1 = 1.0E(5)\,\mathrm{Jmol}^{-1}$, $Q_2 = 5.0E(5)\,\mathrm{Jmol}^{-1}$, $Q_3 = Q_4 = 3.0E(10)\,\mathrm{Jmol}^{-1}$, $M_F = 1.6E(-2)$, $M_{R_1} = 1.5E(-2)$, $M_{R_2} = 1.0E(-2)$, $Y_{R_10} = M_{R_20} = 0.01$, $S = 7.6766E(-2)\,\mathrm{m}^2$, $V = 2.0E(-3)\,\mathrm{m}^3$, $\rho = 0.038\,\mathrm{kgm}^{-3}$, $C_P = 638.5\,\mathrm{Jkg}^{-1}\,\mathrm{K}^{-1}$, $\chi = 39.0798\,\mathrm{Js}^{-1}\,\mathrm{m}^{-2}\,\mathrm{K}^{-1}$, $T_0 = 600\,\mathrm{K}$, $R = 8.31441\,\mathrm{JK/mol}$.

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