

On the Effect of Reaction Order on Stability of Two-Variable Model for Combustion in Sealed Container

A.O. Popoola and R.O. Ayeni

Department of Pure and Applied Mathematics,
Ladoke Akintola University of Technology, Ogbomoso, Nigeria

Abstract: We study a two-step Arrhenius reaction $A \xrightarrow{K_0} X \xrightarrow{K_1} B$ in the multiple-step reaction that occurs during decomposition and combustion processes of a precursor chemical reagent. In order to enhance safety during manufacturing, storage and handling of the energetic materials, we revisit and analyze the equilibrium, stability and Hopf's bifurcation of the two-variable model for combustion in sealed containers and investigate the effect of reaction order on stability of the equilibrium solution. The numerical result of Hopf's bifurcation condition shows that the region of instability increases as the reaction order increases.

Key words: Effect of reaction, stability, two-variable model, combustion, sealed container, Nigeria

INTRODUCTION

The study of solutions of mathematical equations describing some combustion problems has attracted the interest of many researchers (Ayeni *et al.*, 2005; Buckmaster and Ludford, 1992; Chan and Kong, 1995; Derrick and Grossman, 1976; Patrick Folly, 2001; Ganutdinov, 2001; Goldfarb *et al.*, 1999, 2004; Golovaty, 2006; Holmes, 1990; Menikoff, 1999; Powers, 1999; Claire and Larry, 2006). This study in general, has led to the design of new or improved combustion devices.

Explosives (substances that react violently with the liberation of heat and gas) can be classified into homogeneous and heterogeneous. A homogeneous explosive can be gaseous, liquid or single crystal of a solid. Solid explosives are typically heterogeneous for example; TNT pressed to less than full density is heterogeneous due to the presence of voids (Menikoff, 1999). Goldfarb *et al.* (1999, 2004), Buckmaster and Ludford (1992), Powers (1999), Folly (2001) and Menikoff (1999) studied explosives models and obtained some useful results. Holmes (1990) in his remark, stated that explosives are generally useful for blasting, military purposes and as propellant and that the energy released by a chemical explosion generally results from two exothermic reactions, one following the other in rapid succession. The first reaction involves the decomposition of NO_2 to produce N_2 . The second reaction involves the combustion of carbon and hydrogen with oxygen to form

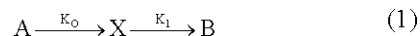
carbon II oxide, carbon IV oxide and water. If large amount of heat is released, the resulting temperature may exceed 5000°C (Holmes, 1990).

Other recent contributors include Trenham and Forbes (2006) who studied the comparison of two and three-variable models for combustion in sealed containers. They established the Hopf's bifurcation conditions for the models and show that self sustained oscillations are found to occur as a result of Hopf's bifurcation. The contributions of Derrick and Grossman (1976) were also helpful to analyze the equilibrium and stability of a first order ordinary differential equation.

In this study, Following the Arrhenius equation of 1889, Chan and Kong (1995) and Trenham and Forbes (2006) new model of combustion in sealed containers are formulated and the effect of reaction order on stability of the model is investigated.

MATHEMATICAL FORMULATION

Following Trenham and Forbes (2006) a precursor chemical species (reagent) A that decays to form an intermediate X and then a final inert product B, is considered such that



Where K_0 is a constant rate and K_1 is the temperature dependent Arrhenius rate. The species A is kept in drums

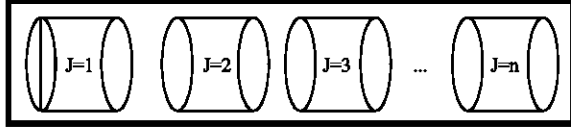


Fig. 1: The sketch of a system of n drums in a sealed container

J=1, 2, ..., n inside a sealed shipping container as shown in Fig. 1.

The Arrhenius temperature sensitive rate for the second reaction is defined as

$$K_1(T) = ZT^m e^{\frac{-E}{RT}}, \quad m \geq 0 \quad (2)$$

Where E is the activation energy, R is the gas constant known as Boltzmann gas constant and T is the temperature in degree Kelvin, Z is the pre-exponential factor and m is a reaction order.

Remark1: The case m = 0 was considered by Trenham and Forbes (2006).

Following (Trenham and Forbes, 2006), the governing equations (the rate equation and conservation of energy for drum number 'j' in a system of n drums) for the model are given by

$$\frac{d[X_j]}{dt} = K_{j0}[A_j] - K_{j1}(T_j)[X_j] \quad (3)$$

$$\rho_j c_j V_j \frac{dT_j}{dt} = Q_j m_j^w V_j [X_j] K_{j1}(T_j) + X_j S_j (T_D - T_j), \quad j = 1, 2, \dots, n \quad (4)$$

Supplemented by the conservation of energy for the entire container to give

$$\rho_D c_D V_D \frac{dT_D}{dt} = \sum_{j=1}^n \chi_j S_j (T_j - T_D) - \chi_D S_D (T_D - T_a) \quad (5)$$

Where k_{j0} = rate of constant step for each drum, $k_{j1}(T_j)$ = Exothermic rate given in Eq. 3. c_j = specific heat capacity of the material in each drum. ρ_j = density, m_j^w = molecular weight, $[A_j]$ = concentration of the pool chemical A, Q_j = exothermic heating term, χ_j = Newtonian cooling coefficient representing energy/degree/area/time, V_j = volume of each drum, S_j = surface area of each drum. In the supplemented energy equation for the entire container, other system parameters include ρ_D = density, c_D = specific heat capacity, V_D = volume, S_D = surface area.

Non-dimensionalization: The above equations are non-dimensionalized by using these suitable parameters;

$$\alpha_g = \frac{\rho_D c_D V_D}{\rho_1 c_1 V_1}, \beta_D = \frac{X_D S_D}{X_1 S_1}, \mu_1 = k_{10} \tau_s, \\ \theta_a = \frac{RT_a}{E_1}, \lambda_1 = \frac{X_1 S_1 E_1}{V_1 Q_1 m_1^w [A_1] Z_1 R} \text{ and } n$$

Where α_g represents a volume and specific heat ratio between the container and any of the drums, β_D represents a surface area ratio between the container and the drums, μ_1 represents a non-dimensional rate term dependent on the reaction, the scaled ambient temperature θ_a is a non-dimensional temperature of the environment outside the container and λ_1 is the heat transfer coefficient between the drums and the container, n is the number of drums in the container, and the reference time

$$\tau_s = \frac{\rho_1 c_1 E_1}{Q_1 m_1^w [A_1] Z_1 R}$$

(Trenham and Forbes, 2006). It is also noted that

$$T_1 = \frac{T}{T_a}, T_a = \frac{E_1}{R}.$$

The model becomes

$$\frac{dX_1}{dt} = \mu_1 - X_1 (\theta_a T_1)^m e^{\frac{-1}{T_1}} \quad (6)$$

$$\frac{dT_1}{dt} = X_1 (\theta_a T_1)^m e^{\frac{-1}{T_1}} + \lambda_1 (T_D - T_1) \quad (7)$$

$$\alpha \frac{dT_D}{dt} = n \lambda_1 (T_1 - T_D) - \beta \lambda_1 (T_D - \theta_a) \quad (8)$$

By quasi-equilibrium assumption for T_D

$$T_D \approx \left(\frac{n}{n + \beta_D} \right) T_1 + \frac{\beta_D \theta_a}{n + \beta_D} \quad (9)$$

$$\frac{dX_1}{dt} = \mu_1 - X_1 (\theta_a T_1)^m e^{\frac{-1}{T_1}} \quad (10)$$

$$\frac{dT_1}{dt} = X_1 (\theta_a T_1)^m e^{\frac{-1}{T_1}} - \frac{\beta_D \lambda_1}{n + \beta_D} (T_1 - \theta_a) \quad (11)$$

Equilibrium analysis: For equilibrium,

$$\frac{dX_1}{dt} = \frac{dT_1}{dt} = 0$$

and this leads to the equilibrium point

$$(X_{1e}, T_{1e}) = \left(\mu_1 (\theta_a T_{1e})^{-m} e^{\frac{1}{T_{1e}}}, \theta_a + \frac{\mu_1 (n + \beta_D)}{\beta_D \lambda_1} \right) \quad (12)$$

$$\Rightarrow (X_{1e}, T_{1e}) = \left(\begin{array}{c} \mu_1 \exp \left(\frac{\beta_D \lambda_1}{\theta_a \beta_D \lambda_1 + \mu_1 (n + \beta_D)} \right) \\ \left(\theta_a^2 + \frac{\mu_1 (n + \beta_D) \theta_a}{\beta_D \lambda_1} \right)^{-m}, \theta_a + \frac{\mu_1 (n + \beta_D)}{\beta_D \lambda_1} \end{array} \right) \quad (13)$$

Stability analysis: We re-write the Eq. (10) and (11) as

$$\left. \begin{array}{l} \frac{dX_1}{dt} = f(X_1, T_1) \\ \frac{dT_1}{dt} = g(X_1, T_1) \end{array} \right\} \quad (14)$$

Where

$$\left. \begin{array}{l} f(X_1, T_1) = \mu_1 - X_1 (\theta_a T_1)^m e^{\frac{1}{T_1}} \\ g(X_1, T_1) = X_1 (\theta_a T_1)^m e^{\frac{1}{T_1}} - \frac{\beta_D \lambda_1}{n + \beta_D} (T_1 - \theta_a) \end{array} \right\} \quad (15)$$

By Taylor's series expansions of $f(X_1, T_1)$ and $g(X_1, T_1)$

$$f(X_1, T_1) = f(X_{1e}, T_{1e}) + \frac{\partial f}{\partial X_1} (X_{1e}, T_{1e}) X_1 + \frac{\partial f}{\partial T_1} (X_{1e}, T_{1e}) T_1 + \dots \quad (16)$$

$$g(X_1, T_1) = g(X_{1e}, T_{1e}) + \frac{\partial g}{\partial X_1} (X_{1e}, T_{1e}) X_1 + \frac{\partial g}{\partial T_1} (X_{1e}, T_{1e}) T_1 + \dots \quad (17)$$

The 4 partial derivatives in the expansions are

$$\frac{\partial f}{\partial X_1} (X_1, T_1) = -(\theta_a T_1)^m e^{\frac{1}{T_1}} \quad (18)$$

$$\frac{\partial f}{\partial T_1} (X_1, T_1) = -X_1 \theta_a^m T_1^{m-1} \left(m + \frac{1}{T_1} \right) e^{\frac{1}{T_1}} \quad (19)$$

$$\frac{\partial g}{\partial X_1} (X_1, T_1) = (\theta_a T_1)^m e^{\frac{1}{T_1}} \quad (20)$$

$$\frac{\partial g}{\partial T_1} (X_1, T_1) = X_1 \theta_a^m T_1^{m-1} \left(m + \frac{1}{T_1} \right) e^{\frac{1}{T_1}} - \frac{\beta_D \lambda_1}{n + \beta_D} \quad (21)$$

$$\text{At equilibrium, } f(X_{1e}, T_{1e}) = g(X_{1e}, T_{1e}) = 0 \quad (22)$$

Then the Eq. (16) and (17) become

$$f(X_1, T_1) = -(\theta_a T_{1e})^m e^{\frac{1}{T_{1e}}} X_1 - X_{1e} \theta_a^m T_{1e}^{m-1} \left(m + \frac{1}{T_{1e}} \right) e^{\frac{1}{T_{1e}}} T_1 + \dots \quad (23)$$

$$g(X_1, T_1) = (\theta_a T_{1e})^m e^{\frac{1}{T_{1e}}} X_1 + \left(X_{1e} \theta_a^m T_{1e}^{m-1} \left(m + \frac{1}{T_{1e}} \right) e^{\frac{1}{T_{1e}}} - \frac{\beta_D \lambda_1}{n + \beta_D} \right) T_1 + \dots \quad (24)$$

In matrix form, we have

$$\begin{pmatrix} f(X_1, T_1) \\ g(X_1, T_1) \end{pmatrix} = \begin{pmatrix} -(\theta_a T_{1e})^m e^{\frac{1}{T_{1e}}} & -X_{1e} \theta_a^m T_{1e}^{m-1} \left(m + \frac{1}{T_{1e}} \right) e^{\frac{1}{T_{1e}}} \\ (\theta_a T_{1e})^m e^{\frac{1}{T_{1e}}} & X_{1e} \theta_a^m T_{1e}^{m-1} \left(m + \frac{1}{T_{1e}} \right) e^{\frac{1}{T_{1e}}} - \frac{\beta_D \lambda_1}{n + \beta_D} \end{pmatrix} \begin{pmatrix} X_1 \\ T_1 \end{pmatrix} + \begin{pmatrix} f_1(X_1, T_1) \\ g_1(X_1, T_1) \end{pmatrix} \quad (25)$$

Following Derricks and Grossman (1976)

$$\lim_{(X_1, T_1) \rightarrow (X_{1e}, T_{1e})} \frac{f_1(X_1, T_1)}{\sqrt{X_1^2 + T_1^2}} = \lim_{(X_1, T_1) \rightarrow (X_{1e}, T_{1e})} \frac{g_1(X_1, T_1)}{\sqrt{X_1^2 + T_1^2}} = 0 \quad (26)$$

$$\text{Let } A = \begin{pmatrix} -(\theta_a T_{1e})^m e^{\frac{1}{T_{1e}}} & -X_{1e} \theta_a^m T_{1e}^{m-1} \left(m + \frac{1}{T_{1e}} \right) e^{\frac{1}{T_{1e}}} \\ (\theta_a T_{1e})^m e^{\frac{1}{T_{1e}}} & X_{1e} \theta_a^m T_{1e}^{m-1} \left(m + \frac{1}{T_{1e}} \right) e^{\frac{1}{T_{1e}}} - \frac{\beta_D \lambda_1}{n + \beta_D} \end{pmatrix} \quad (27)$$

The characteristic equation $|A - \sigma I| = 0$ implies that

$$\begin{vmatrix} -(\theta_a T_{1e})^m e^{\frac{-1}{T_{1e}}} - \sigma & -X_{1e} \theta_a^m T_{1e}^{m-1} \left(m + \frac{1}{T_{1e}}\right) e^{\frac{-1}{T_{1e}}} \\ (\theta_a T_{1e})^m e^{\frac{-1}{T_{1e}}} & \left(X_{1e} \theta_a^m T_{1e}^{m-1} \left(m + \frac{1}{T_{1e}}\right) e^{\frac{-1}{T_{1e}}} - \frac{\beta_D \lambda_1}{n + \beta_D} \right) \end{vmatrix} - \sigma = 0 \quad (28)$$

$$\Rightarrow \sigma^2 - T_j \sigma + D_j = 0 \quad (29)$$

where $T_j = (\theta_a T_{1e})^m e^{\frac{-1}{T_{1e}}} \left(\frac{X_{1e}}{T_{1e}} \left(m + \frac{1}{T_{1e}}\right) - 1 \right) - \frac{\beta_D \lambda_1}{n + \beta_D}$ (30)

$$D_j = (\theta_a T_{1e})^m e^{\frac{-1}{T_{1e}}} \frac{X_{1e}}{T_{1e}} \left(m + \frac{1}{T_{1e}}\right) + \frac{\beta_D \lambda_1}{n + \beta_D} - X_{1e} \theta_a^m T_{1e}^{m-1} \left(m + \frac{1}{T_{1e}}\right) \quad (31)$$

The Eq. 29 gives

$$\Rightarrow \sigma = \frac{1}{2} \left(T_j \pm \sqrt{T_j^2 - 4D_j} \right) \quad (32)$$

The stability of equilibrium point is determined by the sign of T_j when $D_j > 0$ and $T_j^2 < 4D_j$;

1. Stable focus occurs for $T_j < 0$
 2. Unstable focus occurs for $T_j > 0$
 3. Hopf's bifurcation occurs for $T_j = 0$
- (33)

Hopf's bifurcation analysis: For Hopf's bifurcation, $T_j = 0$ when $D_j > 0$

$$\Rightarrow T_j = (\theta_a T_{1e})^m e^{\frac{-1}{T_{1e}}} \left(\frac{X_{1e}}{T_{1e}} \left(m + \frac{1}{T_{1e}}\right) - 1 \right) - \frac{\beta_D \lambda_1}{n + \beta_D} = 0 \quad (34)$$

$$\Rightarrow (\theta_a T_{1e})^m e^{\frac{-1}{T_{1e}}} \left(\frac{X_{1e}}{T_{1e}} \left(m + \frac{1}{T_{1e}}\right) - 1 \right) = \frac{\beta_D \lambda_1}{n + \beta_D} \quad (35)$$

$$\left(\theta_a^2 + \frac{\mu_1 (n + \beta_D) \theta a}{\beta_D \lambda_1} \right)^m e^{\frac{-\beta_D \lambda_1}{\mu_1 (n + \beta_D) + \theta a \beta_D \lambda_1}} - \frac{m \mu_1 \beta_D \lambda_1}{\mu_1 (n + \beta_D) + \theta a \beta_D \lambda_1} - \frac{\mu_1 (\beta_D \lambda_1)^2}{(\mu_1 (n + \beta_D) + \theta a \beta_D \lambda_1)^2} + \frac{\beta_D \lambda_1}{n + \beta_D} = 0 \quad (36)$$

The Eq. 36 is the Hopf's bifurcation condition for the two-variable system.

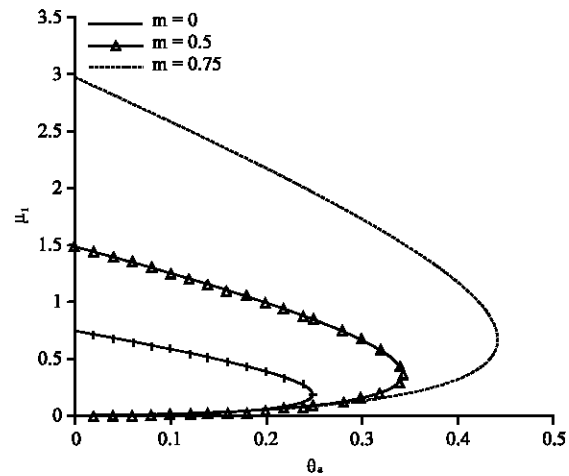


Fig. 2: Hopf's bifurcation curve $T_j = 0$ for fixed values of $\lambda_1 = 0.9$, $\beta_D = 9$, $n = 2$ and various values of reaction order $m < 1$

RESULTS AND DISCUSSION

By using Maple software, the numerical result for $T_j = 0$, the Hopf's condition (36), which is the point at which the stability changes is presented as Fig. 2.

The equilibrium, stability and Hopf's bifurcation analyses have led to the establishment of certain criteria. The Eq. (13) shows the equilibrium point while the criteria for stability of the equilibrium point have been established in Eq. (33). A criterion for Hopf's bifurcation has also led to the establishment of Hopf's condition (36). The numerical solution of the Hopf's condition shows that the region of instability increases as the order of reaction (m) increases.

CONCLUSION

This result is expected not only be useful to regulate and improve the chain reaction mechanism but will enhance safety during manufacturing, storage and handling of the energetic material.

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