



MATHEMATICAL MODELLING OF TWO-STEP EXOTHERMIC REACTIONS WITH AND WITHOUT REACTANTS CONSUMPTION

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ABSTRACT

This paper studies two-step exothermic reactions with and without reactants consumption subject to Arrhenius kinetics model. The resulting system of equations modelling the physical problem is coupled non-linear ordinary differential equations. Analytical investigations are possible based on some classical Frank-Kamenetskii criteria. Exact analytical expressions are derived for temperatures and ignition times based on the assumption of without reactants consumption. Thereafter, the entire system of equations is solved numerically to account for effect of various dimensionless parameters with reactants consumption. The numerical solutions, graphs and the statistical measures of skewness and kurtosis for dimensionless concentrations η and γ , and temperature θ profiles are presented in this work.

Keywords: Two-step Arrhenius kinetics, reactant consumption, analytical expressions, skewness and kurtosis measures.

AMS Subject Classification 2000: 03C50, 03C65

NOMENCLATURE

English symbols

c_p Specific heat at constant pressure
($JK^{-1}kg^{-1}$)

E_i activation energies ($J/kmol$)

F_i pre-exponential factors ($1/s$)

Q_i heat of reactions (J/kg)

R universal gas constant ($Jkmol^{-1}K^{-1}$)

r ratio of activation energies

T temperature (K)

t_r characteristic time

X concentration of reactant A ($kg/kmol$)

Y concentration of reactant B ($kg/kmol$)

Greek Symbols

ρ density (kg/m^3)

β dimensionless activation energy

τ dimensionless time

θ dimensionless temperature of the reactants

η dimensionless concentration of reactant A

γ dimensionless concentration of reactant B

Subscript

$i = 1, 2$

P pressure

INTRODUCTION

In a number of cases, several different products may be produced simultaneously from a single initial reactant. In these circumstances, the reaction leading to formation of various products may take place either in parallel or in succession (Frank-Kamenetskii, 1969). The study of non-premixed spontaneous ignition in the coflow-mixing layer, with a one-step Arrhenius model

adopted for the chemistry, was performed by Linan and Crespo (1976), who took advantage of large value of activation energy typically of combustion process for their asymptotic analysis. They found that the evolution of reactive mixing layers is characterized by an initial quasi-frozen stage in which the two streams mix and begin to react, followed by a sudden explosion or thermal runaway that clearly identifies the ignition location. Nunziato *et al.* (1977) derived an expression for thermal Ignition time of a homogeneous explosive which is exothermally decomposing by two parallel Arrhenius reactions under the assumption of constant thermo-physical properties and Frank-kamenetskii approximation of the Arrhenius term. Ayeni (1982) presented as asymptotic analysis of a spatially homogeneous model of non-isothermal branched-chain reaction. Of particular interest is the so-called explosion time and he provided an upper bound for it as a function of the activation energy which can vary over all positive values. The analysis of Aldler and Herbert (1985) examined the phase plane solutions of dimensionless temperature as functions of dimensionless reactant depletion for a first-order well-stirred reaction. A new criterion for criticality was introduced and shown to be consistent in the Semenov limit and to give parametric values at which criticality disappears. In Okoya (1999), the author derived an analytic expression for the thermal ignition time of a reactive system. He employed effective activation energy approach, which allows the elimination of previous difficulties arising in the estimate of ignition time. The result of the novel technique is compared with numerical result as well as those obtained previously and there is good agreement. Varatharajan and Williams (2000) proposed the concept of branched-chain thermal explosions on the well-known hydrogen-oxygen reaction which have traditionally exhibited the two distinct phenomena of branched-chain and thermal explosions. They employed Frank-kamenetskii type asymptotic and obtained expressions for ignition times. In another development, Popoola and Ayeni (2005) investigated the dependency of activation energies of a two-step Arrhenius reaction, in which the unsteady and steady cases

of a two-step Arrhenius reaction were considered and the relationship between the activation energies of the chain reaction was assumed. Study on the behaviour of a single initial reactant producing different products simultaneously subject to two-step Arrhenius kinetic was modelled by Adegbe *et al.* (2005). The model is transient, one-dimensional and includes the effects of activation energies on the explosion time and maximum temperature of the reactant. Adegbe and Alao (2006) studied a premixed reactive mixture of oxidizer and fuel reacting exothermally subjected to one-step Arrhenius kinetics. Theorem on the existence of unique solution of the problem was formulated and proved. Analytical expressions for the thermal ignition time t_i , with and without reactant consumption, under the assumptions of constant thermo-physical properties and Frank-Kamenetskii approximation of large activation energy were derived. In general, the problem formulated was solved numerically when the new parameter λ is strictly greater than modified characteristic time δ . Sidhu *et al* (2009) undertook a numerical investigation of travelling nonadiabatic combustion waves for the case of a two-step chain branching reaction mechanism. For simplicity, they assumed equal diffusivity of the reactant, radicals and heat. The speed of the combustion wave was analysed for different values of the heat loss parameter and how the extinction limit depends on the heat loss parameter as well as properties of the fuel were determined.

The purpose of this study is to derive analytical expressions for ignition time and temperature of two-step exothermic reactions when the reactants consumption is neglected. Consequently, when contribution of the reactant consumption (i.e. reactant depletion) is taken into consideration the resulting system of equations, which highly nonlinear and coupled, is solved numerically to account for effect of various dimensionless parameters. The numerical solutions, graphs and the statistical measures of skewness and kurtosis for dimensionless concentrations η and γ , and temperature θ profiles are featured promptly in this work.

Mathematical Formulation of the Problem

Two-step exothermic reactions subjected to Arrhenius kinetics model is considered. The basic model scheme follows from simple chemistry of sequential reaction, which can be described by the following equation:



We assume that the initial reactant A participates in two parallel reactions



with activation energies E_1 and E_2 , and heats of reaction Q_1 and Q_2 , respectively, which are widely different (Adegbe et al., 2005). The main physical assumptions of the suggested model are the following:

- i. spatially homogeneous approach is applied,
- ii. the dependence of the pre-exponent factor on the temperature is ignored,
- iii. the change in density in different parts of the vessel is neglected, and
- iv. the thermal conductivity of the walls are regarded as infinitely large.

Under these assumptions, the system of governing equations reads as follows

$$\frac{dX}{dt} = -F_1 X \exp(-E_1 / RT) \quad (4)$$

$$\frac{dY}{dt} = -F_2 Y \exp(-E_2 / RT) \quad (5)$$

$$\rho c_p \frac{dT}{dt} = F_1 Q_1 X \exp(-E_1 / RT) + F_2 Q_2 Y \exp(-E_2 / RT) \quad (6)$$

The system (4)–(6) includes concentration equations for reactants A and B , and energy balance equation for the reactants, respectively. Initial conditions for the system:

$$X(0) = X_0, Y(0) = Y_0, T(0) = T_0. \quad (7)$$

Non-dimensional Analysis

In this study, in order to reduce the number of parameters in the system of equations (4)–(6) we introduce the following dimensionless variables:

$$\left. \begin{aligned} \theta &= \frac{T - T_0}{\varepsilon T_0}, \quad \beta = \frac{RT_0}{E_1}, \quad \tau = \frac{t}{t_r}, \quad r = \frac{E_2}{E_1}, \\ t_r &= \frac{\exp(1/\beta)}{F_1}, \quad \eta = \frac{X}{X_0}, \quad \gamma = \frac{Y}{Y_0}. \end{aligned} \right\} \quad (8)$$

Therefore, using (8) in (4)–(7), the dimensionless system of governing equations has the following form:

$$\frac{d\eta}{d\tau} = -\eta \exp\left(\frac{\theta}{1+\beta\theta}\right) \tag{9}$$

$$\frac{d\gamma}{d\tau} = -\alpha \gamma \exp\left(\frac{r\theta}{1+\beta\theta}\right) \tag{10}$$

$$\frac{d\theta}{d\tau} = \delta_1 \eta \exp\left(\frac{\theta}{1+\beta\theta}\right) + \delta_2 \gamma \exp\left(\frac{r\theta}{1+\beta\theta}\right) \tag{11}$$

with initial conditions

$$\eta(0) = 1, \quad \gamma(0) = 1, \quad \theta(0) = 0. \tag{12}$$

In equations (9) – (11), the following dimensionless parameters have been introduced:

$$\alpha = \frac{F_2}{F_1} \exp\left(\frac{1}{\beta}(1-r)\right), \tag{13}$$

$$\delta_1 = \frac{Q_1 X_0}{\rho c_p \beta T_0}, \tag{14}$$

$$\delta_2 = \frac{F_2 Q_2 Y_0}{F_1 \rho c_p \beta T_0} \exp\left(\frac{1}{\beta}(1-r)\right). \tag{15}$$

Analytical Analysis

In this section, we shall investigate reduced system of ordinary differential equations governing the physical model based on the following realistic assumptions:

- (a) The reaction rate depends only on the temperature in accordance with $\exp(-E/RT)$ i.e., we neglect the consumption of reactants, which means that $\eta = 1$ and $\gamma = 1$.
- (b) Frank-Kamenetskii approximation $\exp\left(\frac{\theta}{1+\beta\theta}\right) \approx \exp(\theta)$ is considered as $\beta \rightarrow 0$.

Following the assumptions above, the system of equations (9) – (12) reduces to

$$\left. \begin{aligned} \frac{d\theta}{d\tau} &= \delta_1 \exp(\theta) + \delta_2 \exp(r\theta) \\ \theta(0) &= 0 \end{aligned} \right\} \tag{16}$$

Case 1: $E_1 = E_2$

When the activation energies of the sequential reactions are equal, equation (16) becomes

$$\left. \begin{aligned} \frac{d\theta}{d\tau} &= (\delta_1 + \delta_2) \exp(\theta) \\ \theta(0) &= 0. \end{aligned} \right\} \tag{17}$$

Integrating equation (17), we obtain the temperature of the reactants as $\theta = -\ln[1 - (\delta_1 + \delta_2)\tau]$ and the ignition time is $\tau = 1/(\delta_1 + \delta_2)$ as $\theta \rightarrow \infty$.

Case 2: $E_1 = -E_2$

When the activation energies of the sequential reactions are equal but alternate negatively, equation (16) becomes

$$\left. \begin{aligned} \frac{d\theta}{d\tau} &= \delta_1 \exp(\theta) + \delta_2 \exp(-\theta) \\ \theta(0) &= 0 \end{aligned} \right\} \quad (18)$$

Integrating equation (18), we obtain $\theta = \frac{1}{2} \ln \left\{ \left(\frac{\delta_2}{\delta_1} \right) \tan \left[\sqrt{\delta_1 \delta_2} \tau + \tan^{-1} \left(\frac{\sqrt{\delta_1 \delta_2}}{\delta_2} \right) \right]^2 \right\}$ and the required

ignition time as $\theta \rightarrow \infty$ is $\tau = \frac{1}{\sqrt{\delta_1 \delta_2}} \left\{ \frac{\pi}{2} - \tan^{-1} \left(\sqrt{\frac{\delta_1}{\delta_2}} \right) \right\}$.

Table 1: Comparison of exact and numerical solutions for cases 1 and 2

Case 1				Case 2		
τ	θ Exact	θ Numerical	Error	θ Exact	θ Numerical	Error
0	0	0	0	0	0	0
0.1	0.013085	0.013000	8.5×10^{-5}	0.013020	0.013000	2.0×10^{-5}
0.2	0.026344	0.026170	1.74×10^{-4}	0.026081	0.026040	4.1×10^{-5}
0.3	0.039781	0.039515	2.66×10^{-4}	0.039186	0.039123	6.3×10^{-5}
0.4	0.053401	0.053039	3.62×10^{-4}	0.052337	0.052250	8.7×10^{-5}
0.5	0.067209	0.066747	4.62×10^{-4}	0.065537	0.065425	1.12×10^{-4}
0.6	0.081210	0.080644	5.66×10^{-4}	0.078787	0.078649	1.38×10^{-4}
0.7	0.095410	0.094736	6.74×10^{-4}	0.092091	0.091925	1.66×10^{-4}
0.8	0.109815	0.109028	7.87×10^{-4}	0.105452	0.105256	1.95×10^{-4}
0.9	0.124430	0.123525	9.05×10^{-4}	0.118871	0.118645	2.26×10^{-4}
1.0	0.139262	0.138235	1.028×10^{-3}	0.132351	0.132093	2.58×10^{-4}

Numerical Analysis

The system of coupled non-linear ordinary differential equations (9) – (12) is not tractable to exact (analytical) methods of solution. Therefore, a numerical scheme based on finite difference approximation is employed to solve the system of equations. In order to ascertain this numerical technique, we compare the exact solutions of the cases 1 and 2 with the numerical solutions of the cases 1 and 2. The results in the Table 1 are in good agreement. Hence, the resulting finite difference approximation schemes for the system of equations (9) – (12) are:

$$\eta_{i+1} = \eta_i - h\eta_i \exp\left(\frac{\theta_i}{1 + \beta\theta_i}\right) \quad (19)$$

$$\gamma_{i+1} = \gamma_i - h\alpha\gamma_i \exp\left(\frac{r\theta_i}{1 + \beta\theta_i}\right) \quad (20)$$

$$\theta_{i+1} = \theta_i + h \left\{ \delta_1 \eta_i \exp\left(\frac{\theta_i}{1 + \beta\theta_i}\right) + \delta_2 \gamma_i \exp\left(\frac{r\theta_i}{1 + \beta\theta_i}\right) \right\} \quad (21)$$

$$\eta_0 = 1, \quad \gamma_0 = 1, \quad \theta_0 = 0. \quad (22)$$

Consequently, we present numerical computations of the schemes (19) –(22) in Figures 1–6 for various values of activation energies ratio r and dimensionless activation energy β when α , δ_1 , δ_2 are fixed.

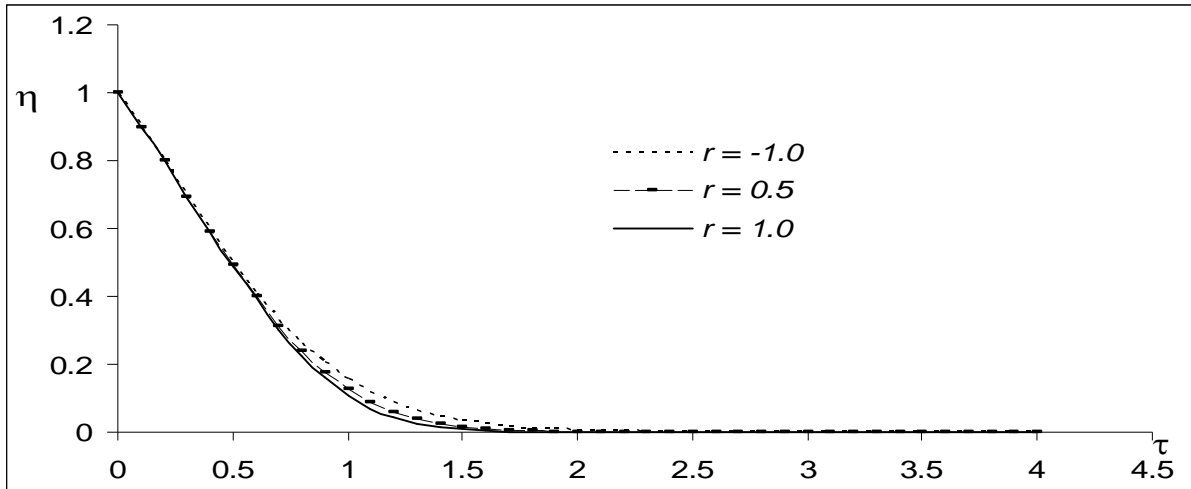


Figure 1: Graph of η with time for various values of r when $\delta_1 = 0.8$, $\delta_2 = 0.5$, $\alpha = 0.5$, $\beta = 0.05$.

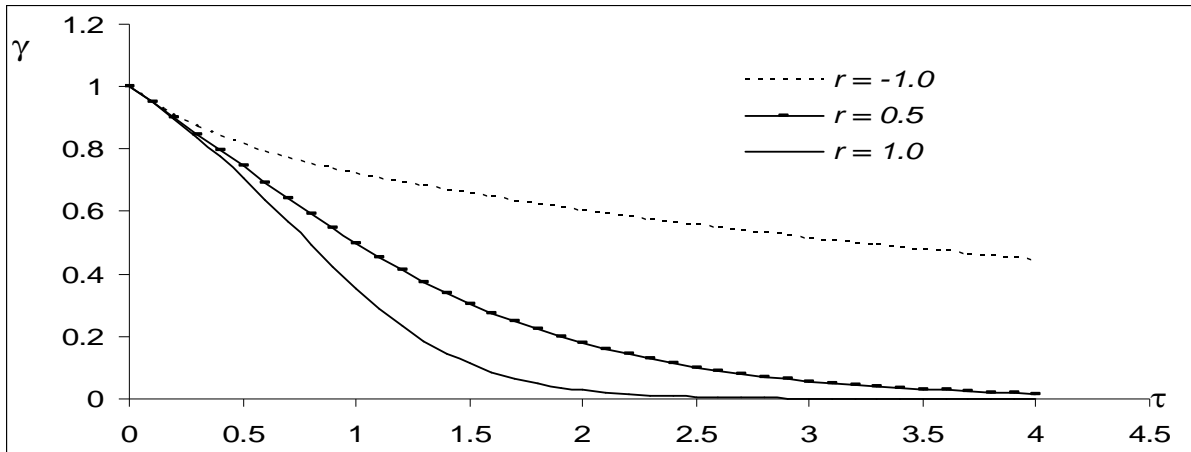


Figure 2: Graph of γ with time for various values of r when $\delta_1 = 0.8$, $\delta_2 = 0.5$, $\alpha = 0.5$, $\beta = 0.05$.

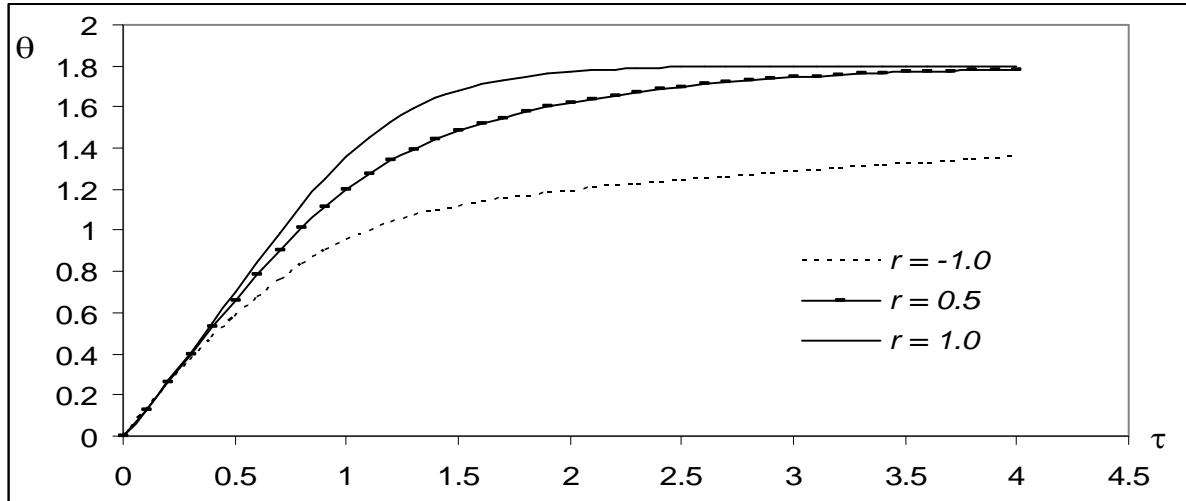


Figure 3: Graph of θ with time for various values of r when $\delta_1 = 0.8$, $\delta_2 = 0.5$, $\alpha = 0.5$, $\beta = 0.05$.

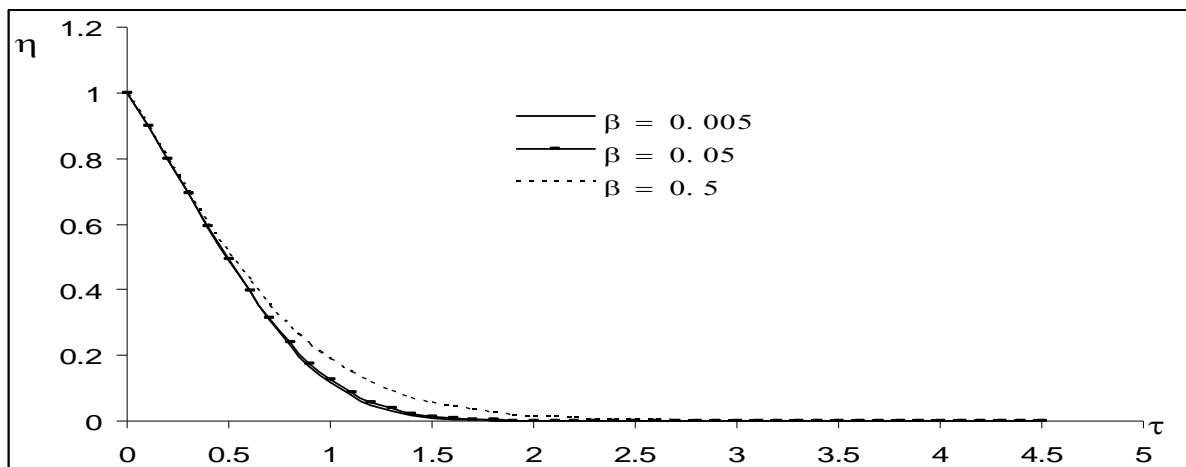


Figure 4: Graph of η with time for various values of β when $\delta_1 = 0.8$, $\delta_2 = 0.5$, $\alpha = 0.5$, $r = 0.5$.

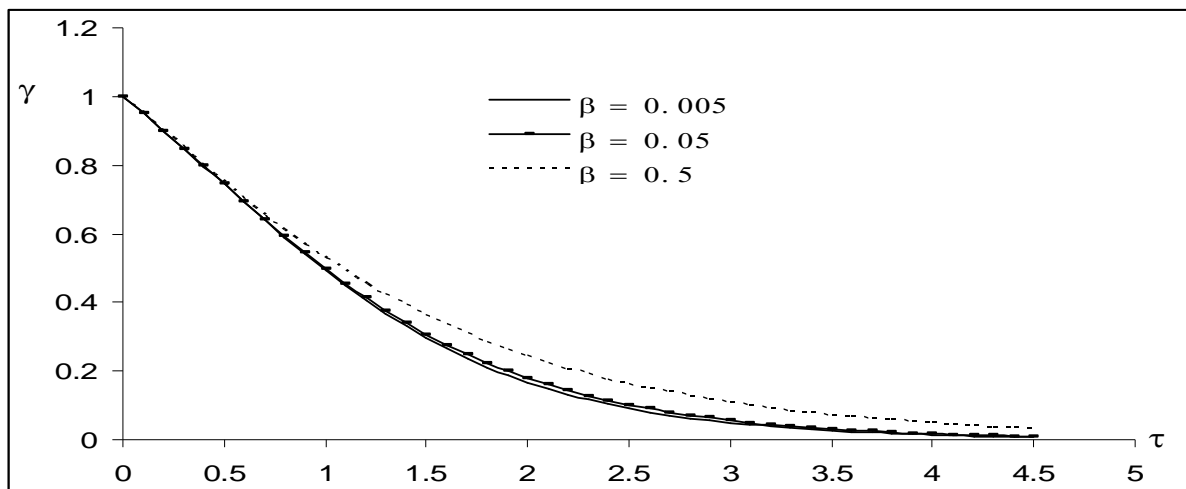


Figure 5: Graph of γ with time for various values of β when $\delta_1 = 0.8$, $\delta_2 = 0.5$, $\alpha = 0.5$, $r = 0.5$.

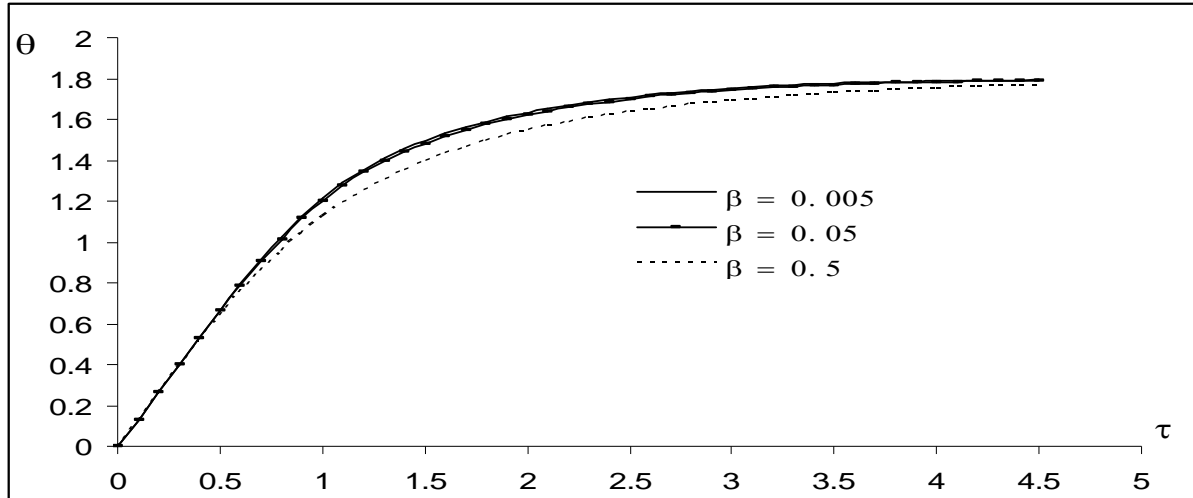


Figure 6: Graph of θ with time for various values of β when $\delta_1 = 0.8$, $\delta_2 = 0.5$, $\alpha = 0.5$, $r = 0.5$.

Table 2: Descriptive statistics of variation of η with activation energy and activation energies ratio parameters

Skewness				Kurtosis			
r	Statistic	β	Statistic	r	Statistic	β	Statistic
-1.0	1.922	0.005	1.992	-1.0	2.663	0.005	2.896
0.5	1.976	0.05	1.976	0.5	2.842	0.05	2.842
1.0	2.003	0.5	1.854	1.0	2.930	0.5	2.439

Table 3: Descriptive statistics of variation of γ with activation energy and activation energies ratio parameters

Skewness				Kurtosis			
r	Statistic	β	Statistic	r	Statistic	β	Statistic
-1.0	0.777	0.005	0.966	-1.0	0.170	0.005	-0.368
0.5	0.926	0.05	0.952	0.5	-0.418	0.05	-0.379
1.0	1.329	0.5	0.820	1.0	0.351	0.5	-0.477

Table 4: Descriptive statistics of variation of θ with activation energy and activation energies ratio parameters

Skewness				Kurtosis			
r	Statistic	β	Statistic	r	Statistic	β	Statistic
-1.0	-1.575	0.005	-1.432	-1.0	1.628	0.005	0.931
0.5	-1.419	0.05	-1.419	0.5	0.904	0.05	0.904
1.0	-1.606	0.5	-1.329	1.0	1.331	0.5	0.717

DISCUSSION OF RESULTS

In this study, we present exact analytical expressions for temperatures and ignition times for the following cases $r = -1$ and $r = 1$ when reactants consumption is neglected. Moreover, Table 1 shows the comparison of exact and numerical solutions of dimensionless temperature. It is obvious from the Table 1 that the results are in good agreement. This comparison informs us that the numerical scheme based on finite difference approximation is appropriate to solve the entire system of equations.

Consequently, we present numerical solutions of the entire system of coupled non-linear ordinary differential equations based on finite difference approximation schemes. The general characteristic features of Figures 1–6 show time histories of dimensionless concentration of reactants A and B , (i.e. η and γ), and dimensionless temperature θ with various values of dimensionless activation energies ratio r and activation energy β parameters when $\delta_1 = 0.8$, $\delta_2 = 0.5$, $\alpha = 0.5$. The qualitative impacts of these dimensionless parameters in this study are ascertained in the Figures below. We notice in Figures 1–2 that increase in the value of activation energies ratio r causes spontaneous depletion in η and γ , respectively. This reveals that the rate of consumption of the concentration of the reactants depend on activation energies ratio. Meanwhile in Figure 3, it is observed that increase in the value activation energies ratio r raises the temperature of the reactants. Figures 4–5 reveal that increase in the value the activation energy appreciates significantly the rate of consumption of concentration of reactants η and γ , respectively, whereas in Figure 6 it reduces the temperature of the reactants. This depicts that activation energy contribute extensively to depletion of the reactant consumption and temperature, respectively.

In an experiment of measuring X , Y and T (or its dimensionless version η , γ and θ), it is often pertinent to look into the distributional attributes of each of these quantities. To this, we conduct measure of skewness and dispersion. Skewness (which is a measure of symmetry, or more precisely, the lack of symmetry of experimental outcomes of η , γ and θ which are symmetric if each of them looks the same to the left and right of the center point). The distribution of each of X , Y and T possesses characterises its attributes. For normally distributed quantities, coefficient of skewness is zero with kurtosis value of three. The detailed analyses of these statistical measures are given in Tables 2–4. It is seen that η and γ are right skewed while temperature θ is left skewed (negatively skewed) irrespective of the value of r and β as reaction time grows. Similarly, for the measure of kurtosis (which is a measure of whether the results got are peaked or flat relative to a normal distribution. That is, data sets with high kurtosis tend to have a distinct peak near the mean, decline rather rapidly, and have heavy tails) is presented in Tables 2–4. The three distributions are not peaked and hence the three quantities are strictly non-normal in geometry.

CONCLUSION

This study had delved into the mathematical modelling of two-step exothermic sequential reactions with and without reactant depletion. The mathematical formulation involves a system of three highly coupled non-linear ordinary differential equations which was reduced to one equation and solved analytically based on realistic assumptions. Analytical expressions were derived for temperature of the reactants and ignition times without depletion when the activation energie are equal and alternate negatively, respectively. Moreover, the entire system of equations was solved numerically by finite difference approximation scheme. In addition, statistical analysis based on measures of skewness and kurtosis enunciated that

concentration of the reactants and temperature of the reactants were strictly non-normal in geometry. The study revealed that the rate of reactants depletion and temperature of reactants of two-step exothermic sequential reactions could be control by activation energies ratio and activation energy paramters, respectively. The results highlighted above are useful in both explosion and combustion industries for regulations and safety purposes.

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