

Reaction Kinetics Model of Polymerization in the Absence of Material Diffusion

Durojaye M.O. and Ayeni R.O.

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

Abstract

This paper is on reaction kinetics models for approximating diffuse propagation reaction fronts in one-dimensional gasless combustion type models. This study is carried out in the context of free-radical frontal polymerization (FP) via a propagating, self sustaining reacting front in the absence of material diffusion.

The model which is a system of partial differential equations is linearized into a system of ordinary differential equations and solved numerically. Results are obtained for different values of \mathcal{E} .

Keywords: Frontal polymerization, Material diffusion.

1. Background and Introduction

Frontal polymerization is a mode of free-radical polymerization of a monomer which in the presence of a thermally unstable initiator converts into a polymer via a propagating, localized reaction zone. (Comissiong et al, 2005).

In a typical experiment the reagents are put in a glass tube, and the temperature of the mixture increased by applying a heat source at the top of the tube. The increase in temperature induces decomposition of the initiator which produces active radicals, and the polymer chain growth process begins. Chemical conversion then occurs in a narrow, localized region. Depending on the choice of the reactants and the conditions of the experiment, the front either may or may not propagate with a constant speed. Various non-uniform propagation can occur, if it is assumed that the front always remain flat. The polymer chain growth occurring in this reaction zone is highly exothermic, and the resulting heat release promotes initiator decomposition ahead of the front. In this way, a self sustained reaction wave can form (Golovaty, 2007). This unusual method of polymerization holds promise as a method of producing currently available materials in a more energy-efficient process, and of producing superior thermoset materials.

There are several conditions necessary for the existence of the frontal mode. First the ignition temperature must be high enough to generate and initially sustain the reaction front. Further, the reaction rate must be extremely small at the initial (ambient) temperature but very large at the front temperature. The high reaction rate coupled with the exothermicity of the reaction must be sufficient to overcome heat losses into the reactants and product zones.

Both steady and unsteady front propagation have been observed in many research works. Unsteady front propagation is usually undesirable as it leads to the non-uniform “layered” structure of the final product. One of the goals of the modeling is to determine the range of material parameters within which the stability of uniformly propagating polymerization front is guaranteed. The analysis of the full model is, however too complicated because it requires solving a system of coupled nonlinear partial differential equations describing multiple reactions and energy transport. In order to make analytical predictions, numerous simplifications are usually introduced by employing asymptotics in terms of small parameters, considering effective kinetics, etc. This difference in parameter values may lead to the differences in observable long time behaviors between systems undergoing self propagation high-temperature synthesis (SHS) and frontal polymerization (FP) (Golovaty, 2007).

2. Reaction Kinetics Model In The Absence Of Material Diffusion

Although the mechanism of free radicals polymerization involves three steps – initiation, propagation, and termination – and five reagents – an initiator, and active initiator radical, an active polymer radical, a monomer, and a complete polymer chain, a number of simplifying assumptions are made to reduce the complexity of the underlying mathematical mode (Golovaty, 2007).

Corresponding authors: E-mail: -, Tel. +2348053207468

Hence we assume that:

- The rate of reactions between the initiator radicals and the monomer and between the polymer radicals and the monomer are the same.
- The rate of change of total radical concentration is much smaller than the rate of their production and consumption.
- The initial concentration of the initiator is so large that it is not appreciably consumed during the polymerization process.
- Both reagents and the final product are viscous enough to ignore convective effects and bubble formation.
- The test tube is sufficiently thin with the adiabatic boundary condition on sidewalls is so that the spatial dependence of the solution be restricted to the axial variable.

Supposed that a test tube containing the monomer – initiator mixture occupies a region $\Omega \in R^3$ and denote by $M(x, t)$ the monomer concentration and by $T(x, t)$ the temperature of the mixture at the point $x \in \Omega$ and the time $t \geq 0$ then for the process of free – radical polymerizations, Golovaty presented a single step, effective kinetics model of monomer- to-polymer conversion as

$$\frac{\partial M}{\partial t} = -kMe \frac{E}{R_g T_b} \left(1 - \frac{T_b}{T}\right) \tag{1}$$

$$\frac{\partial T}{\partial t} = \text{div}(\kappa \nabla T) + kqMe \frac{E}{R_g T_b} \left(1 - \frac{T_b}{T}\right) \tag{2}$$

and assume that T and M satisfy the initial conditions

$$T(x, 0) = T_0 \tag{3}$$

$$M(x, 0) = M_0, x \in [-L, L]$$

$$T_x(-L, t) = 0,$$

$$M_x(\pm L, t) = 0, \tag{4}$$

$$T(L, t) = T_b,$$

$$t \in (0, t_0)$$

where: κ is the thermal diffusivity of the mixture/final product

k is the effective pre-exponential factor in the Arrhenius Kinetics

R_g is the gas Constant.

E is the effective activation energy.

T_b is a reference temperature to be specified

c = specific heat density

ρ = mixture density

$$q = -\frac{\Delta H}{c\rho}, \text{ where } \Delta H = \text{reaction enthalpy}$$

Throughout this work, we assume that the test tube is one – dimensional, $\Omega = [-L, L]$, and that thermal diffusivity κ is constant (we ignore possible dependence of κ on temperature and degree of conversion $(1 - M/M_0)$). Then the problem (1) – (2) reduces to

$$\frac{\partial M}{\partial t} = -kMe \frac{E}{R_g T_b} \left(1 - \frac{T_b}{T}\right) \tag{5}$$

$$\frac{\partial T}{\partial t} = \kappa \frac{\partial^2 T}{\partial x^2} + kqMe \frac{E}{R_g T_b} \left(1 - \frac{T_b}{T}\right) \tag{6}$$

We will assume that T and M satisfy the initial conditions

$$\begin{aligned} T(x,0) &= T_0 \\ M(x,0) &= M_0, x \in [-L, L] \end{aligned} \tag{7}$$

In order to initiate the reaction, heat must be supplied to the system; hence for the first t_0 seconds we will use the following boundary conditions

$$\begin{aligned} T_x(-L, L) &= 0, \\ M_x(\pm L, t) &= 0, \\ T(L, t) &= T_b, \\ t &\in (0, t_0) \end{aligned} \tag{8}$$

During the front propagation regime, we impose the adiabatic and impenetrability boundary conditions on the temperature and the monomer concentration, respectively by setting

$$\begin{aligned} T_x(\pm L, t) &= 0, \\ M_x(\pm L, t) &= 0, \\ t &\geq t_0 \end{aligned} \tag{9}$$

3. Nondimensionalization

To facilitate the analysis of the system (5) and (6), we introduce a convenient non-dimensionalization;

Let $\theta = (T - T_b) \frac{E}{R_g T_b^2}$ be a non-dimensional temperature,

We can now write equations (5) and (6) as

$$\frac{\partial M}{\partial t} = -kMe^{\theta/1+\epsilon\theta} \tag{14}$$

$$\frac{\partial \theta}{\partial t} = \kappa \frac{\partial^2 \theta}{\partial x^2} + \delta Me^{\theta/1+\epsilon\theta} \tag{15}$$

Where $\delta = \frac{kE}{R_g T_b^2}$ is the Frank – Kamneskii Parameter.

The initial and boundary conditions are:

$$\begin{aligned} \theta(x,0) &= 0, \\ M(x,0) &= 1, x \in [-l, l] \end{aligned} \tag{16}$$

$$\begin{aligned} M_x(\pm l, t) &= 0 \\ \theta_x(\pm l, t) &= 0, t \geq \tau_0 \\ \theta(l, t) &= 1, t \in (0, \tau_0) \end{aligned} \tag{17}$$

4. Transforming The Model Into A System of Ordinary Differential Equations

We now modify the problem as

$$\frac{\partial M}{\partial t} = M_0 - kMe^{\theta/1+\epsilon\theta} \tag{18}$$

$$\frac{\partial \theta}{\partial t} = \kappa \frac{\partial^2 \theta}{\partial x^2} + \delta Me^{\theta/1+\epsilon\theta} \tag{19}$$

Where M_0 is the initial monomer rate.

According to Sattinger (1972), $\kappa \frac{\partial^2 \theta}{\partial x^2}$ can be approximated as $-\eta\theta$

Using this in equation (19), we have

$$\frac{dM}{dt} = M_0 - kMe^{\frac{\theta}{1+\epsilon\theta}} \tag{20}$$

$$\frac{d\theta}{dt} = -\eta\theta + \delta Me^{\frac{\theta}{1+\epsilon\theta}} \tag{21}$$

$$\theta(x,0) = 0, \\ M(x,0) = 1, x \in [-l, l]$$

5. Existence and Uniqueness of Solution

Theorem 1

Let $\Omega = \{(X, t) : |x_i| \leq c, 0 \leq t \leq d\}$, where $(x_i = x_1, x_2)$, and η, M_0, k and δ are constants, $0 < \epsilon < 1$. Then the initial value problem (20) – (21) has a unique solution.

Proof

Let $x_1 = M, x_2 = \theta$ in eqn (20) and (21)

We take functions f_1, f_2 such that

$$f_1(x_1, x_2) = M_0 - kx_1 e^{\frac{x_2}{1+\epsilon x_2}}$$

$$f_2(x_1, x_2) = -\eta x_2 + \delta x_1 e^{\frac{x_2}{1+\epsilon x_2}}$$

The partial derivatives are:

$$\left| \frac{\partial f_1}{\partial x_1} \right| = \left| -k e^{\frac{x_2}{1+\epsilon x_2}} \right|,$$

$$\left| \frac{\partial f_1}{\partial x_2} \right| = \left| \frac{-kx_1}{(1+\epsilon x_2)^2} e^{\frac{x_2}{1+\epsilon x_2}} \right|$$

$$\left| \frac{\partial f_2}{\partial x_1} \right| = \left| \delta e^{\frac{x_2}{1+\epsilon x_2}} \right|$$

$$\left| \frac{\partial f_2}{\partial x_2} \right| = \left| -\eta + \frac{\delta x_1}{(1+\epsilon x_2)} e^{\frac{x_2}{1+\epsilon x_2}} \right|$$

for $x_2 \geq 0$ we have,

$$\left| \frac{\partial f_1}{\partial x_1} \right| \leq +k$$

$$\left| \frac{\partial f_1}{\partial x_2} \right| \leq +k$$

$$\left| \frac{\partial f_2}{\partial x_1} \right| \leq \delta$$

$$\left| \frac{\partial f_2}{\partial x_2} \right| \leq +\eta + \delta$$

$\Rightarrow \frac{\partial f_1}{\partial x_1}, \frac{\partial f_1}{\partial x_2}, \frac{\partial f_2}{\partial x_1}$ and $\frac{\partial f_2}{\partial x_2}$ are continuous and bounded,

Then by Boyce. 2001. p 105, the boundary value problem (20) – (21) has a unique solution.

6. Numerical Solution

We solve the resulting system of ordinary differential equations (20) – (21) for various values of K for $\mathcal{E} = 0.1$ using MATLAB ode23 solver. See Appendix

The results for different values of k and \mathcal{E} are shown in the following graphs;

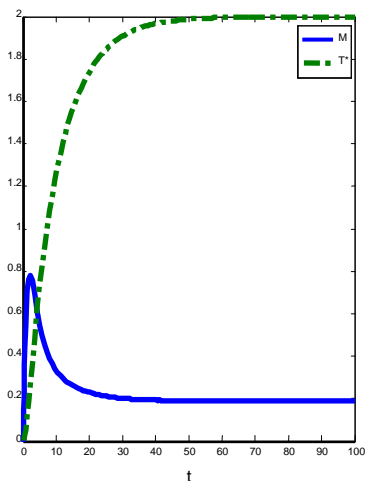


Fig. 1 Graph of $\theta(x,t)$ and $M(x,t)$ against t for $k=1$ and $\mathcal{E}=0.1$

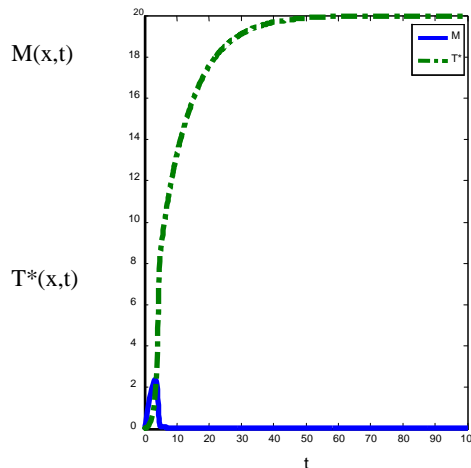


Fig.2 Graph of $\theta(x,t)$ and $M(x,t)$ against t for $k=0.1$ and $\mathcal{E}=0.1$

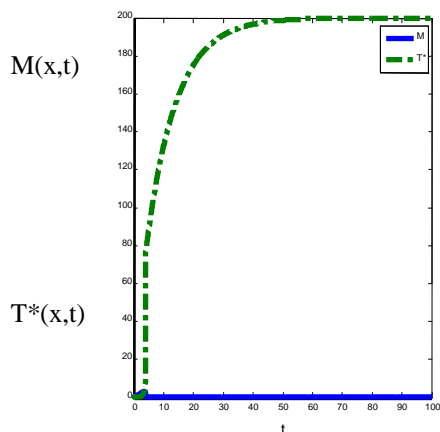


Fig. 3 Graph of $\theta(x,t)$ and $M(x,t)$ against t for $k=0.001$ and $\mathcal{E}=0.1$

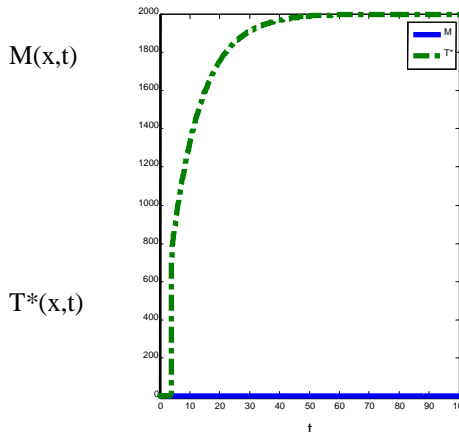


Fig. 4 Graph of $\theta(x,t)$ and $M(x,t)$ against t for $k=0.001$ and $\mathcal{E}=0.1$

7. Discussion of Results

- (i) Figures 1 show that at $k=1$ and when activation energy is small so that $\mathcal{E}=0.1$, monomer concentration rises and decreases after a point while temperature increases with time.
- (ii) Figure 2 show that at $k=0.1$ temperature increases with time while rise in monomer concentration is lower than in figure 1.
- (iii) Figure 3 and 4 show that at $k=0.1$ and $k=0.01$, very little reactant is consumed, while temperature increases with time.

8. Conclusion

- (i) When k small, very little reactant is consumed, while temperature rises with time. in all cases

Appendix

Matlab programme for solving

$$\frac{dM}{dt} = M_0 - kMe^{\frac{\theta}{1 + \epsilon\theta}}, \quad \frac{d\theta}{dt} = -\eta\theta + \delta Me^{\frac{\theta}{1 + \epsilon\theta}}$$

dm(1)= mo-k*m(1)*exp(m(2)/(1+e*m(2)));

dm(2)=-gamma*m(2)+delta*m(1)*exp(m(2)/(1+e*m(2)));

plot(t,m(:,1),'-',t,m(:,2),'-') grid

Title (plot of M and T as functions of time);

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