A Method of Lines Solution of Reaction Kinetics Model of Polymerization in The Presence of Material Diffusion

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Abstract

This paper is on the semianalytical method of lines solution of reaction kinetics model of polymerization in the presence of material diffusion. The approach is to reduce the model partial differential equation to a vector system of ordinary differential equations and solve using standard methods for ordinary differential equations. Using this method we obtained temperature profiles for p = 1, 2, 3 and the time dependent behavior of temperature for all the cases.

1.0   Introduction

The method of lines (MOL) is regarded as a special finite difference method. It involves discretising the spatial domain of a partial differential equation (pde) and thus replacing thepartial differential equation with a vector system of ordinary differential equations (ODEs) that approximates the pde. We can then apply any integration algorithm for initial value ordinary differential equations to compute an approximate numerical solution to the pde.[1].The MATLAB package has strong vector and matrix handling capabilities, a good set of ODE solvers, and an extensive functionality which can be used to implement the MOL one of which is ode15s.

Ode 15s is an implicit numerical differentiation formula of orders 1 to 5 for stiff systems. Ode 15s like any other Matlab ode solvers has a built in local error estimate to control the step size. Moreover it is a variable order package which uses higher order methods and smaller step sizes when the solution varies rapidly [2].

In the rest of the paper, the reaction kinetic model in the presence of material diffusion is presented in section two of the paper. The method of lines solution is presented in section three, section four is on results presentation and discussion and conclusion is found in section five of the paper. The list of references concludes the paper.

2.0   Problem Statement.

Suppose that a test tube containing the monomer – initiator mixture occupies a region $\Omega \in R^3$ with monomer concentration, $M(x,t)$ and, the temperature of the mixture at the point $x \in \Omega$ and the time $t \geq 0$ is $T(x,t)$. Then for a free – radical polymerization, Golovaty [3, 4], presented a single step, effective kinetics model of monomer- to-polymer conversion as

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

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

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and assumed that T and M satisfy the initial conditions

$$T(x,0) = T_0$$
$$M(x,0) = M_0, x \in [-L, L]$$

(3)

$$T_x(-L,t) = 0,$$
$$M_x(\pm L, t) = 0,$$
$$T(L,t) = T_b,$$

(4)

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

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

$q = -\dfrac{\Delta H}{c\rho}$, where ΔH =reaction enthalpy

Assuming that the test tube is one – dimensional, $\Omega = [-L, L]$, and that thermal diffusivity κ is constant (ignoring possible dependence of κ on temperature and degree of conversion $\left(1 - {M}/{M_0}\right)$. Then the problem (1) – (2) reduced to [3]

$$\frac{\partial M}{\partial t} = -kM e^{\frac{E}{R_g T_B}\left(1 - \frac{T_b}{T}\right)}$$

(5)

$$\frac{\partial T}{\partial t} = \kappa \frac{\partial^2 T}{\partial x^2} + kqM\, e^{\frac{E}{R_g T_b}\left(1 - \frac{T_b}{T}\right)}$$

(6)

where T and M satisfy the initial conditions

$$T(x,0) = T_0$$
$$M(x,0) = M_0, x \in [-L, L]$$

(7)

And boundary conditions

$$T_x(-L, L) = 0,$$
$$M_x(\pm L, t) = 0,$$
$$T(L,t) = T_b,$$

(8)

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

Supposing that a test tube containing the monomer – initiator mixture occupies a region $\Omega \in R^3$, let $M(x,t)$ denotethe monomer concentration and $T(x,t)$ the temperature of the mixture at the point $x \in \Omega$ and the time $t \geq 0$ and $\theta = (T - T_b)\dfrac{E}{R_g T_b^2}$ the non-dimensional temperature, Durojaye and Ayeni, (5) presented a reaction kinetics model of polymerization in the presence of material diffusion as

$$\frac{\partial M}{\partial t} = \frac{\partial^2 M}{\partial x^2} - aM^p e^{\theta/1+\varepsilon\theta} \tag{9}$$

$$\frac{\partial \theta}{\partial t} = \frac{\partial^2 \theta}{\partial x^2} + bM^p e^{\theta/1+\varepsilon\theta} \tag{10}$$

where a, b and p are constants
with initial and boundary conditions

$$\theta(x,0) = 0$$

$$\theta_x(0,t) = \theta_x(1,t) = 0$$

$$M(x,0) = 1 - x \tag{11}$$

$$M_x(0,t) = M_x(1,t) = 0$$

Durojaye and Ayeni [5, 6], considered a particular case where a = b, so that combining the equations resulted in

$$\frac{\partial \theta}{\partial t} = \frac{\partial^2 \theta}{\partial x^2} + b(1-\theta)^p e^{\theta/1+\varepsilon\theta} \tag{12}$$

Subject to initial condition

$$\theta(x,0) = 0 \tag{13}$$

and boundary conditions

$$\theta_x(0,t) = 0 \tag{14}$$

$$\theta_x(1,t) = 0 \tag{15}$$

Results on the existence of solution to this pde and properties of solution are given in [5, 6].

Durojaye and Ayeni [6] gave the numerical solution of the problem using the finite difference formula and gave results on the effect of reaction order on temperature. In a further work, Durojaye and Ayeni [7] solved the problem by the Adomian decomposition method showing the distribution of temperature with time for reactions of order 1, 2 and 3. This paper is a further work on [7]. The work solves the equation by the method of lines to show heat distribution in this polymerization reaction in order to obtain the spatial and transient heat flow of the reaction process.

3.0.   Method of Lines Solution.

Using the usual second order central difference approximation for $\dfrac{\partial^2 \theta}{\partial x^2}$, we have [8],

$$\frac{\partial^2 \theta}{\partial x^2} = \frac{\theta_{i+1} - 2\theta_i + \theta_{i-1}}{(\Delta x)^2} + O(\Delta x^2) \tag{16}$$

Substituting in (12) gives

$$\frac{d\theta_i}{dt} = \frac{\theta_{i+1} - 2\theta_i + \theta_{i-1}}{(\Delta x)^2} + b(1-\theta_i)^p e^{\theta_i/1+\varepsilon\theta_i}, \qquad i = 1, 2, \ldots, N-1 \tag{17}$$

Thesecond order approximation for θ_x is given as [9]

$$\theta_x = \frac{\theta_{i+1} - \theta_{i-1}}{2(\Delta x)} + O(\Delta x^2)$$

Applying this to the boundary conditions (14) and (15)we have

$$\theta_{i+1} = \theta_{i-1} \quad i=1 \text{ and } i=N \tag{18}$$

and substituting in (17) gives a system of approximating ordinary differential equations

$$\frac{d\theta_i}{dt} = \frac{2(\theta_{i+1} - \theta_i)}{(\Delta x)^2} + b(1-\theta_i)^p \, e^{\theta_i / 1+\varepsilon\theta_i}, \qquad i = 1$$

$$\frac{d\theta_i}{dt} = \frac{\theta_{i+1} - 2\theta_i + \theta_{i-1}}{(\Delta x)^2} + b(1-\theta_i)^p \, e^{\theta_i / 1+\varepsilon\theta_i}, \qquad i = 2,\ldots, N-1 \qquad (19)$$

$$\frac{d\theta_i}{dt} = \frac{2(\theta_{i-1} - \theta_i)}{(\Delta x)^2} + b(1-\theta_i)^p \, e^{\theta_i / 1+\varepsilon\theta_i}, \qquad i = N$$

which can be written as

$$\dot{\theta}_1 = \frac{1}{(\Delta x)^2}(-2\theta_1 + 2\theta_2) + b(1-\theta_1)^p \, e^{(\theta_1/1+\varepsilon\theta_1)}$$

$$\dot{\theta}_2 = \frac{1}{(\Delta x)^2}(\theta_1 - 2\theta_2 + \theta_3) + b(1-\theta_2)^p \, e^{(\theta_2/1+\varepsilon\theta_2)} \qquad (20)$$

$$\dot{\theta}_3 = \frac{1}{(\Delta x)^2}(\theta_2 - 2\theta_3 + \theta_4) + b(1-\theta_3)^p \, e^{(\theta_3/1+\varepsilon\theta_3)}$$

$$\vdots \qquad \vdots \qquad \qquad \vdots$$

$$\dot{\theta}_{N-1} = \frac{1}{(\Delta x)^2}(\theta_{N-2} - 2\theta_{N-1} + \theta_N) + b(1-\theta_{N-1})^p \, e^{(\theta_{N-1}/1+\varepsilon\theta_{N-1})}$$

$$\dot{\theta}_N = \frac{1}{(\Delta x)^2}(2\theta_{N-1} - 2\theta_N) + b(1-\theta_{N-1})^p \, e^{(\theta_N/1+\varepsilon\theta_N)}$$

This is a tridiagonal system of algebraic equations with initial condition

$$\theta_i(0) = 0$$

The system of ordinary differential equations (ODEs) is then integrated using the Matlab integrator ode15s which is a stiff integrator since the ordinary differential equations in the system are sufficiently stiff [10].

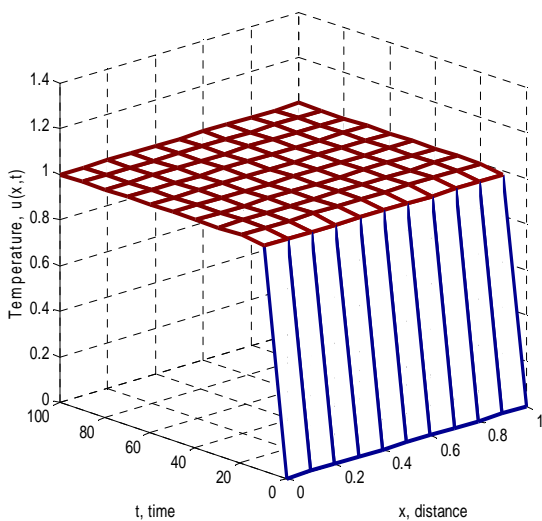## 4.0. Results

Results obtained are as shown on Figures 1 to 6:
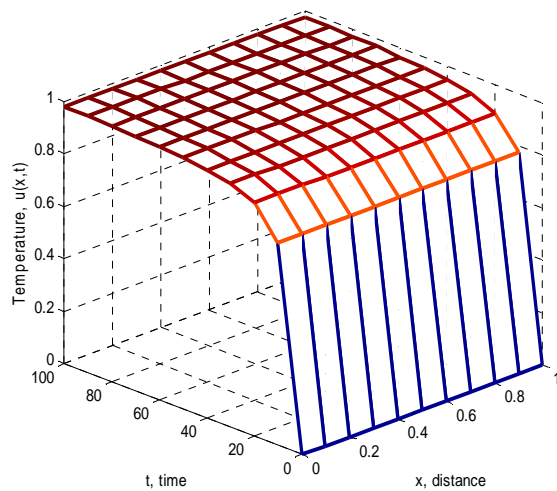

Figure 1   Temperature evolution for p=1, ncall=145

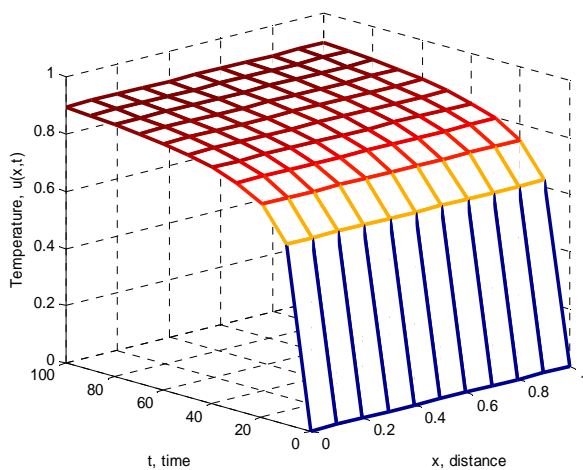Figure 2   Temperature evolution for p=2, ncall=106

Figure 3 Temperature field for p=3, ncall=256
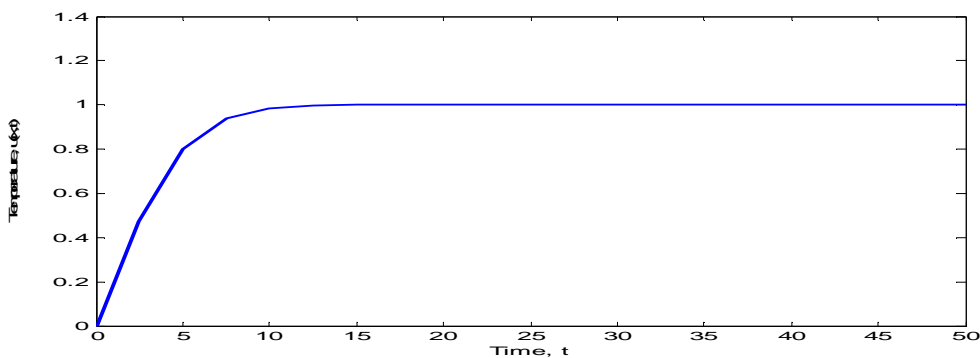

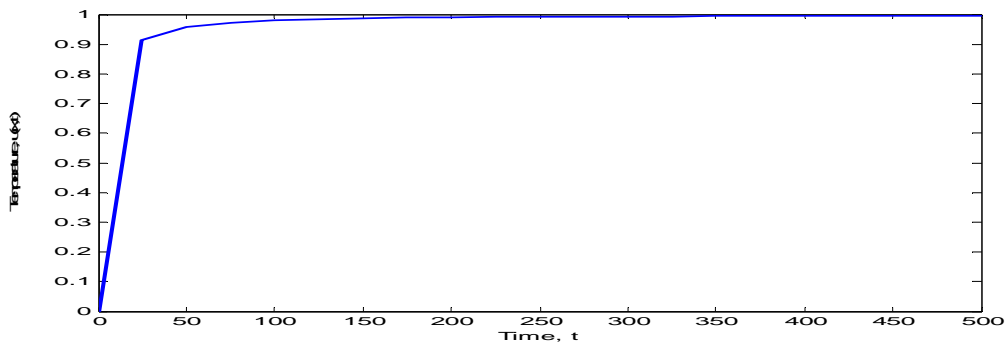Figure 4: Graph of Temperature against time for P=1, t=25, ncall=146

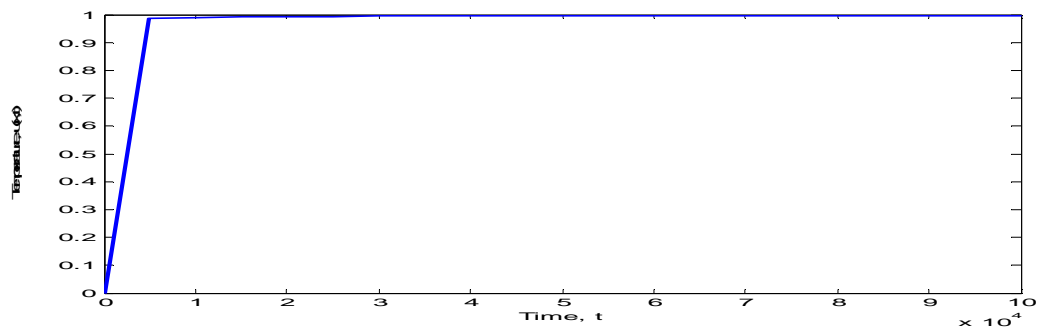Figure 5: Graph of Temperature against time for P=2,t=250, ncall=164

Figure 6: Graph of Temperature against time for P=3, t=50,000, ncall=296

5.0.   Conclusion

We have presented the semi analytical method of lines solution of the reaction kinetics model of polymerization in the presence of material diffusion.

Result shows that for

p=1, the normalized temperature rises from zero and converges to 1 at t=25

P=2, the normalized temperature rises from zero and converges to 1 at t=250

P=3, the normalized temperature rises from zero and converges to 1 at t=50,000

This shows that the time required for the temperature to stabilize in a reaction of lower order is shorter than that required by a reaction of higher order.

It is also observed that the computational effort of the method of lines is quite modest as shown in the number of calls to the ordinary differential equation routine (ncall) for each computation (as shown on each figure).

We therefore conclude that the method of line is a good method for the solution of this problem.

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