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A Numerical Study of Reaction Kinetics Model of Polymerization In The Presence Of Material Diffusion Using the Finite Difference Scheme

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Abstract

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

The model which is a system of partial differential equations is analyzed numerically using the finite difference scheme to obtain results for1, 2, 3, 4, 10, 100, 1000 (where p is the order of reaction).

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 [5].

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 [6]. 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 exhothermicity of the reaction must be sufficient to overcome heat losses into the reactants and product zones.

2. Reaction Kinetics Models In The Presence Of Material Diffusion

Durojaye and Ayeni, [2] presented step function reaction kinetics models of polymerization in the presence of material diffusion and solved analytically using the Adomian decomposition method. In this work we consider the numerical solution using the finite difference scheme,

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

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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, [2] presented step function reaction kinetics models of polymerization in the presence of material diffusion as

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

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

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

$$\begin{aligned} &\theta(x,0) = 0 \\ &\theta_x(0,t) = \theta_x(1,t) = 0 \\ &M(x,0) = 1 - x \\ &M_x(0,t) = M_x(1,t) = 0 \end{aligned} \tag{3}.$$

and considered a particular case where a = b, so that combining the equations we have

$$\frac{\partial \phi}{\partial t} = \frac{\partial^2 \phi}{\partial x^2} \qquad \text{for} \quad \phi = M + \theta \tag{4}$$

with

$$\begin{aligned} &\phi(x,0) = 1 - x \\ &\phi_x(0,t) = \phi_x(1,t) = 0 \end{aligned} \tag{5}$$

Solving by separation of variables we get

$$\phi(x,t) = 1 - \sum_{n=1}^{\infty} \frac{-4}{(2n-1)^2 \pi^2} \cos(2n-1)\pi x e^{(2n-1)^2 \pi^2 t}$$

So, $\phi(x,t) \cong 1$

Therefore we have

$$\frac{\partial \theta}{\partial t} = \frac{\partial^2 \theta}{\partial x^2} + b(1-\theta)^n e^{\theta/1+\varepsilon\theta} \tag{6}$$

$$\begin{aligned} &\theta(x,0) = 0 \\ &\theta_x(0,t) = \theta_x(1,t) = 0 \end{aligned}$$

3. Numerical Solution (Finite Difference Method)

We use the forward difference scheme $\theta_t = \dfrac{\theta_{i,j+1} - \theta_{i,j}}{k}$ and the central difference scheme $\theta_{xx} = \dfrac{\theta_{i+1,j} - 2\theta_{i,j} + \theta_{i-1,j}}{h^2}$ for the time derivative and the space derivative respectively in equation (6) to get

$$\frac{\theta_{i,j+1} - \theta_{i,j}}{k} = \frac{\theta_{i+1,j} - 2\theta_{i,j} + \theta_{i-1,j}}{h^2} + b(1-\theta_{i,j})^p e^{\frac{\theta_{i,j}}{1+\varepsilon\theta_{i,j}}} \tag{7}$$

which can be written as

$$\theta_{i,j+1} = (1-2r)\theta_{i,j} + r(\theta_{i+1,j} + \theta_{i-1,j}) + bk(1-\theta_{i,j})^p e^{\theta_{i,j}/1+\varepsilon\theta_{i,j}}$$

where $r = k/h^2$

We approximate the Neumann boundary condition $\theta_x(0,t)=0$ as

$$\theta_{1,j}=\theta_{-1,j} \tag{8}$$

Also, approximating the Neuman boundary condition $\theta_x(1,t)=0$ in the same way gives

$$\theta_{n,j}=\theta_{n-1,j} \tag{9}$$

Hence our difference scheme is

$$\theta_{i,\,j+1}=\theta_{i,\,j}+\frac{k}{h^2}\left[\theta_{i,\,j+1}-2\theta_{i,\,j}+\theta_{i,\,j+1}\right]+bk(1-\theta)^p\, e^{\theta_{i,j}/1+\varepsilon\theta_{i,j}} \tag{10}$$

$$\theta_{0,j}=0=\theta_{n,j},\quad j=1,2,3,\ldots,n$$

$$\theta_{1,j}=\theta_{0,j}\qquad \theta_{1,j}=\theta_{-1,j}$$

$$\theta_{n,j}=\theta_{n-1,j}\qquad \theta_{n+1,j}=\theta_{n-1,j}\qquad ,0\le r\le \tfrac{1}{2}$$

Lemma 1
The solution of the difference scheme (10) converges point wise to the solution of the initial-boundary value problem (6).

Proof
Following [7] denote the exact solution to the problem (6) by

$$\theta'=\theta'(x,t) \tag{11}$$

and set

$$Z_{k,n}=\theta_{k,n}-\theta'(k\Delta x,n\Delta t)$$

we can write the equation (6) as

$$\theta'_X(k\Delta x,n\Delta t)-\theta'_{XX}(k\,\Delta x,\ n\,\Delta t)-b(1-\theta')^p\, e^{\theta'/1+\varepsilon\theta'}$$

$$=\frac{\theta'_{n+1,k}-\theta'_{n,k}}{\Delta t}-\frac{1}{\Delta x^2}\left(\theta'_{n,k+1}-2\theta'_{n,k}+\theta'_{n,k-1}\right) \tag{12}$$

$$-b(1-k\Delta\theta')^p\, e^{k\Delta\theta'/1+\varepsilon k\Delta t'}+0(\Delta t)+0\left(\Delta x^2\right).$$

Thus, $\theta'_{n,k}=\theta'(k\Delta x,\,n\Delta t)$ satisfies

$$\theta'_{k,n+1}=(1-2r)\theta'_{n,k}+r\left(\theta'_{n,k+1}+\theta'_{n,k-1}\right)$$
$$-b\left(1-\theta'_{n,k}\right)^p e^{\theta'_{n,k}/1+\varepsilon\theta'_{n,k}}+0\left(\Delta t^2\right)+0\left(\Delta t\,\Delta x^2\right) \tag{13}$$

Subtracting (13) from (10), we see that $Z_{n,k}$ satisfies

$$Z_{k,n+1} = (1-2r)Z_{n,k} + r\left(Z_{n,k+1} + Z_{n,k-1}\right) + 0\left(\Delta t^2\right) + 0\left(\Delta t\,\Delta x^2\right). \quad (14)$$

If $0 \le r \le \frac{1}{2}$, the coefficients on the right hand side of (14) are non-negative and

$$\left|Z_k^{n+1}\right| \le (1-2r)\left|Z_k\right| + \left|Z_{n,k+1}\right| + A\left(\Delta t^2 + \Delta t\,\Delta x^2\right) \quad (15)$$

where *A* is the constant associated with the order of terms and depends on the assumed bounds of the higher order derivatives of θ'.

Let

$$Z^n = \sup_k \left|Z_k^n\right|. \quad (16)$$

Then, taking the super mum over *k* yields

$$Z^{n+1} \le Z^n + A\left(\Delta t^2 + \Delta t\ \Delta x^2\right). \quad (17)$$

Applying (17) repeatedly yields

$$Z^{n+1} \le Z^0 + (n+1)\,A\left(\Delta t^2 + \Delta t\ \Delta x^2\right)$$

Since $Z^0 = 0$,

$$\left|\theta_{n-1,k} - \theta'\left(k\Delta x,\ (n+1)\Delta t\right)\right| \le Z^{n+1}$$

and

$$(n+1)\Delta t \to t$$

$$\left|\theta_{n+1,k} - \theta'\left(k\,\Delta x,\ (n+1)\Delta t\right)\right| \le (n+1)\,\Delta t\,A\left(\Delta t + \Delta x^2\right) \to 0 \text{ as } \Delta t,\ \Delta x \to 0.$$

Thus, we see that for any *x* and *t*, as Δt and Δx approach 0 such that $\left(k\Delta x, (n+1)\Delta t\right) \to (x,t)$, $\theta_{n,k}$ approaches $\theta'(x,t)$. This completes the proof.

Lemma 2

The difference scheme (10) is stable.

Proof

The calculation is essentially the same as that done for convergence. We consider any sequence of partitions of the intervals [0,1] defined by the sequence of increments $\{\Delta xj\}$ and the associated spaces, $\{x_j\}$, and norms, $\{\|\cdot\|_j\}$.

Specifically, we choose the space x_j to be the space of $\left(M_{j-1}\right)$ vectors where $M_j \Delta_{xj} = 1$ and let $\|\cdot\|_j$ denote the sup. norm on x_j. As we did earlier, we note that if $r \le \frac{1}{2}$,

$$\begin{aligned} \left|U_k\right|^{n+1} &= \left|(1-2r)U_k^n + r\left(U_{k+1}^n + U_{k-1}^n\right)\right| \\ &= \left|(1-2r)\right|U_k^n\right| + r\left|U_{k+1}^n\right| + r\left|U_{k-1}^n\right| \quad (18) \\ &= \left\|U^n\right\|_k. \end{aligned}$$

Then, taking the maximum over *k* on both sides give us

$$\left\|U^{n+1}\right\|_j \le \left\|U^n\right\|_j \quad (19)$$

If we apply inequality (19) repeatedly, we arrive at

$$\left\|U^{n+1}\right\|_j \le \left\|U^0\right\|_j, \quad (20)$$

Therefore, the difference scheme is stable.

4. Numerical Solution

Applying the Neuman boundary condition $\theta_x(0,t)=0$ and $\theta_x(1,t)=0$, we can write the difference scheme for $i=0$, and $i=n$ respectively as

$$\theta_{0,\,j+1} = \theta_{0,\,j} + \frac{2k}{h^2}\left[\theta_{1,\,j} - \theta_{0,\,j}\right] + bk\,(1-\theta_{i0\,j})^{p}\, e^{\theta_{0,\,j}/1+\varepsilon\theta_{0,\,j}}$$

$$\theta_{n,\,j+1} = \theta_{n,\,j} + \frac{2k}{h^2}\left[\theta_{n+1,\,j} - \theta_{n,\,j}\right] + bk\,(1-\theta_{n,\,j})^{p}\, e^{\theta_{n,\,j}/1+\theta_{n,\,j}}$$

A Pascal program was written to solve this scheme. (See Appendix)
The results for p=1, 2, 3, 4, 10, 100, 1000 and various values of ε is as shown:

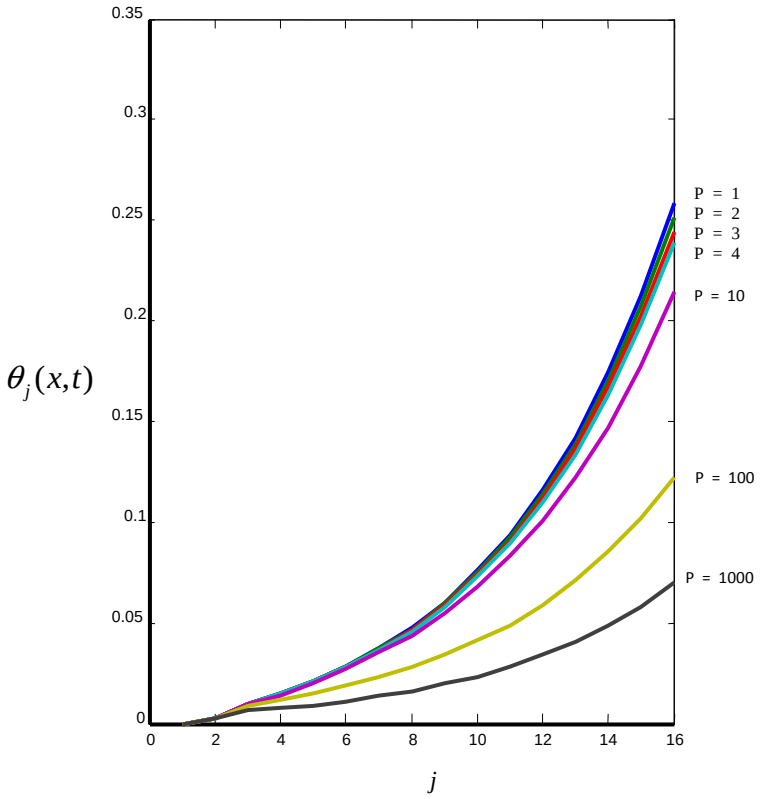

Figure 3.25 Graph of $\theta_j(x,t)$ for p=1, 2, 3,4, 10, 100, 1000 at ε=0.1, x=0.5

5. Conclusion

We have conducted a numerical study of reaction kinetics model of polymerization in the presence of material diffusion with a particular focus on the reaction temperature using the finite difference scheme.

1. We have shown that the solution of the difference scheme converges point wise to the solution of the initial value problem.
2. We established that the numerical scheme is stable.
3. We showed that the reaction order significantly affects the unsteady solution.
4. We showed that the higher the reaction order, the lower the temperature required for the reaction.

Appendix

Pascal Programme For Solving The Difference Scheme (10)

```
program UNSteady(input,output); Type value=array [0..1,0..100] of real; var X:array [0..10] of real; i,j:integer; k,h:real; Q,Y:value;
const epsilon=0.01; b=0.8; n=1;m=4;
Procedure calculate; begin initialise; for j:=0 to 10 do begin for i:=1 to 4 do begin
    Q[i, 1] := k*(Q[i+1, 0]+Q[i-1, 0])/sqr(h)+k*b;
     Q[0, j+1] :=k*(2*Q[1, j]-2*Q[0, j])/sqr(h)+Q[0, j]+k*b*(1-Q[0, j])*exp(Q[0, j]/(1+epsilon*Q[0, j]));
    Q[i, j+1] := k*(1+Q[i+1, j]-2*Q[i, j]+Q[i-1, j])/sqr(h)+Q[i, j]+k*b*(1-Q[i, j])*exp((Q[i, j]+1)/(1+epsilon*Q[i, j]));
      end; end; end;
writeln; write('The otput of the computation is presented'); writeln('for i:=0 to 10 and j:=0'); write('to 15 as below:-'); writeln;
writeln; for i:=0 to 4 do write(i:6); writeln;
   calculate; writeout; readln; End
```

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