COMSOL Multiphysics (Femlab): Unsteady Diffusion-Reaction in Catalysts

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Introduction

Diffusion and chemical reaction inside a porous catalyst is discussed by Bird et. al. ,1960. A comprehensive discussion of catalytic processes is given by Bartholomew et. al., 2005.

When a spherical catalyst particle is originally operating at steady state with a surface concentration boundary condition $C(\xi = 1) = C_1$, and suddenly the surface composition is changed to C_2, the equation (Papadopolous, 2001) describing the change in Γ is

$$\frac{\partial \Gamma}{\partial \tau} = \frac{1}{\xi^2} \frac{\partial}{\partial \xi} \left[\xi^2 \frac{\partial \Gamma}{\partial \xi} \right] - \beta^2 \Gamma \qquad (1)$$

where ξ = r/R
R = radius of sphere - m
τ = tD/R^2
t = time - s
D_s = Diffusivity – m^2/s
β^2 = k_1R^2/D_s
k_1 = first order reaction rate constant – 1/sec

Γ = deviation concentration from an original steady-state concentration (also called = GG)

Defined as $\Gamma(\xi, \tau) = C(\xi, \tau) - C_{ss1}(\xi)$

$C_{ss1}(\xi) = C_1 \sinh(\beta\xi) /(\xi \sinh(\beta))$ and (2)

$C_{ss2}(\xi) = C_2 \sinh(\beta\xi) /(\xi \sinh(\beta))$

where C is concentration

The boundary conditions are

$\Gamma(\tau = 0) = 0$

$\Gamma(\xi = 0)$ = finite for all τ

$\Gamma(\xi = 1) = \Gamma_0$ with $\Gamma_0 = C_2 - C_1$

Using LaPlace transforms Papadopoulos, 2001 presented the following solution to Eq (1) :

$$\frac{\Gamma(\xi,\tau)}{\Gamma_0} = \frac{C(\xi,\tau) - C_{ss1}(\xi)}{C_2 - C_1} = \frac{\sinh(\beta\xi)}{\xi\sinh(\beta)} + \frac{2\pi}{\xi}\sum_{n=1}^{\infty}\frac{(-1)^n\ n\sin(n\pi\xi)}{n^2\ \pi^2 + \beta^2}\ e^{-(n^2\ \pi^2 + \beta^2)\tau} \qquad (3)$$

As originally presented, Eq. (3) had a '-' sign in front of the infinite series. However, Papdopoulos ,2006 showed that Eq. 32.148 in Spiegel's Table ,1968 which was used in the development of Eq . (3) had left off a '-' sign.

In order to evaluate Eq. (2) when $\xi = 0$ L'Hospital's rule can be used:

$$C_{ss1}(0) = C_1 * \frac{\beta}{\sinh(\beta)} \qquad (4)$$

$$C_{ss2}(0) = C_2 * \frac{\beta}{\sinh(\beta)}$$

It is the purpose of this study to evaluate Eq. (3) and Eq. (4) numerically and compare the solution to that obtained by COMSOL Multiphysics, 2005a.

The Spreadsheet Solution

Fig. (1) is the Excel VBA function *totx* used to evaluate the infinite series in Eq. (3).

Eq. (3) becomes indeterminate when $\xi = 0$. When $\xi = 1$ the value of $\frac{\Gamma(\xi,\tau)}{\Gamma_0} = 1$ for all values of τ including 0, which contradicts the boundary condition. As a result Eq. (3) also becomes indeterminate at $\tau = 0$.

At a time greater than 0, the surface concentration of the particle is changed and Eq.(3) can be evaluated numerically for $\tau > 0$.

Fig. (2) is a plot of $\Gamma(\xi, \tau)$ at a time instantly after $\tau = 0$ (i. e., 0.000001). The infinite series for each point generally converged with n (the number of terms evaluated in the series) equal to about 2000. *The value of β is set to 2.5.*

To study Eq. (3) (and Eq. (4)) set τ = *0.048.*

The initial and final steady state composition profiles C_{ss1} and C_{ss2} are calculated from Eq. (2) (and Eq. (4)) and Γ (ξ, τ) is evaluated from Eq. (3) Fig. (3) shows a portion of the spreadsheet which results.

Fig. (4) is a plot of Γ (ξ, τ) (at $\tau = 0.048$) and Fig. (5) is a plot of the concentrations C_{ss1} (ξ) , C_{ss2} (ξ) and C(ξ, 0.048). Fig (6) is a concentration [C(ξ,τ))] vs time (τ) plot at $\xi = 0.1$. The concentration starts out equal to $C_{ss1}(0.1)$ but by $\tau = 0.3$ it is equal to $C_{ss2}(0.1)$.

The COMSOL Multiphysics Solution

It will be assumed that the catalyst pellet is spherically symmetric. By doing this two space coordinates are eliminated and this makes the problem one-dimensional.

The independent variable ξ will be called rh (r/R) and the dependent variable Γ will be called GG.

In order to enter Eq (1) into COMSOL Multiphysics the coefficient form is utilized. The general form (COMSOL Modeling Guide, 2005b) reads:

$$e_a \frac{\partial^2 u}{\partial t^2} + d_a \frac{\partial u}{\partial t} + \nabla \circ (-c \nabla u - \alpha u + \gamma) + \beta \nabla u + \text{a u} = \text{f} \qquad (4)$$

If Eq. (1) is multiplied through by ξ^2 then the following will apply:

$e_a = 0$
t $= \tau$
$d_a = \xi^2$
c $= \xi^2$
$\alpha = 0$
$\gamma = 0$
a $= \beta^2$
f $= 0$

u = GG

The general boundary condition is of the form h * u = rr. For this problem h = 1 and rr = 0 at the $\xi = 0$ boundary and rr = C_2 - C_1 at the $\xi = 1$ boundary.

Model Navigator

1. Open the **Model Navigator.** Click the **Multiphysics** button and click the **Add**

Geometry button.

2. The **Add Geometry** dialog box appears. In the **Space Dimension** list select **1D** and in the **Independent variables** field enter **rh theta phi**. In the **Unit system** list select **none**. Click **OK.**

3. In the list of application modes select:

   COMSOL Multiphysics>PDE Modes> PDE, Coefficient Form>Time-dependent analysis . (Do not click **OK**).

4. Go to the **Dependent variables** field and enter **GG.**

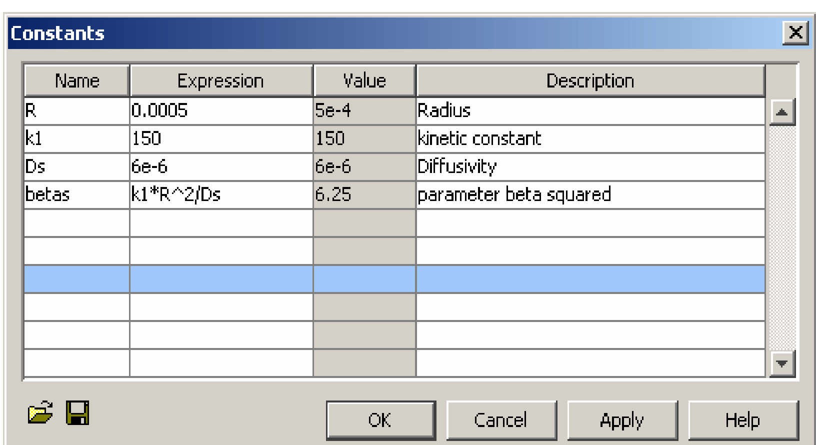
5. In the **Application mode name** edit field enter **Catalyst.**

6. In the **Element** list verify that **Lagrange – Quadratic** is selected.

7. Click **Add (**under Multiphysics**)**, then click **OK.**

Options and Settings

1. From the **Options** menu select **Constants**. Enter the following:



Constants

Name	Expression	Value	Description
R	0.0005	5e-4	Radius
k1	150	150	kinetic constant
Ds	6e-6	6e-6	Diffusivity
betas	k1*R^2/Ds	6.25	parameter beta squared

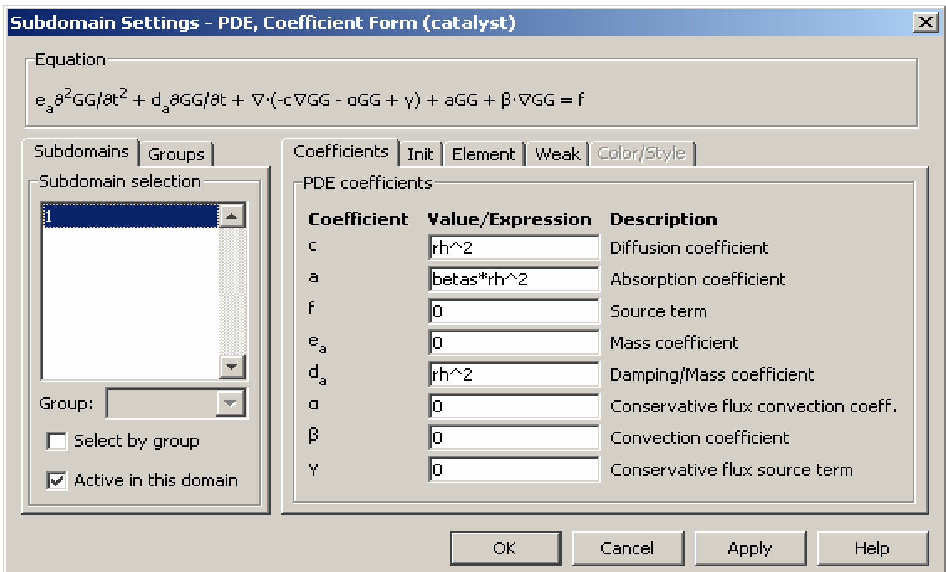
Geometry Modeling

1. Select the menu item **Draw>Specify Objects>Line.**
2. In the **rh** edit field enter **0 1**, then click OK

Physics Settings

Subdomain Settings

1. From the **Physics** menu select **Subdomain Settings.**
2. Go to the **Subdomain** selection and choose **1**. Enter the following:



3. Click **OK**

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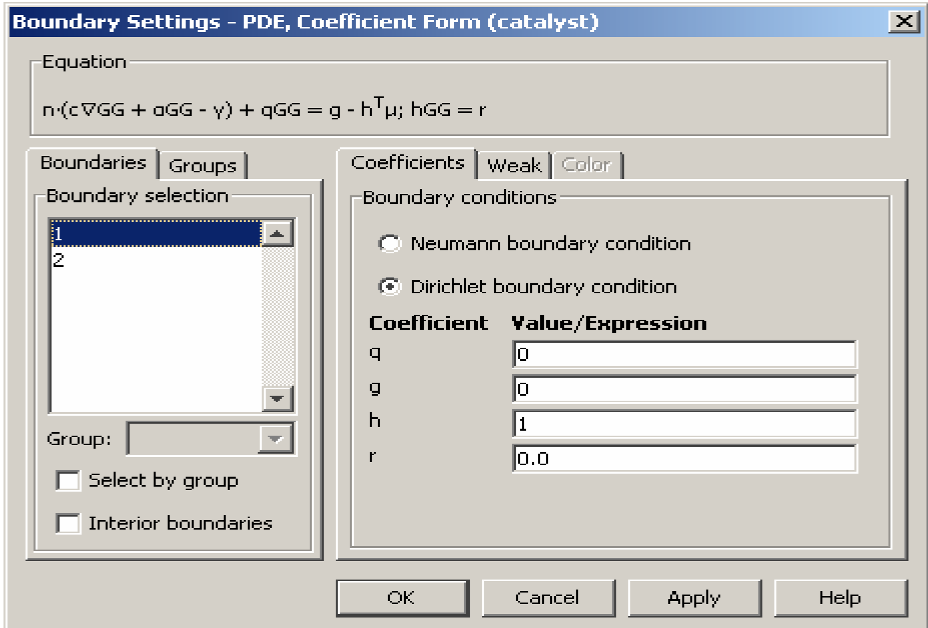
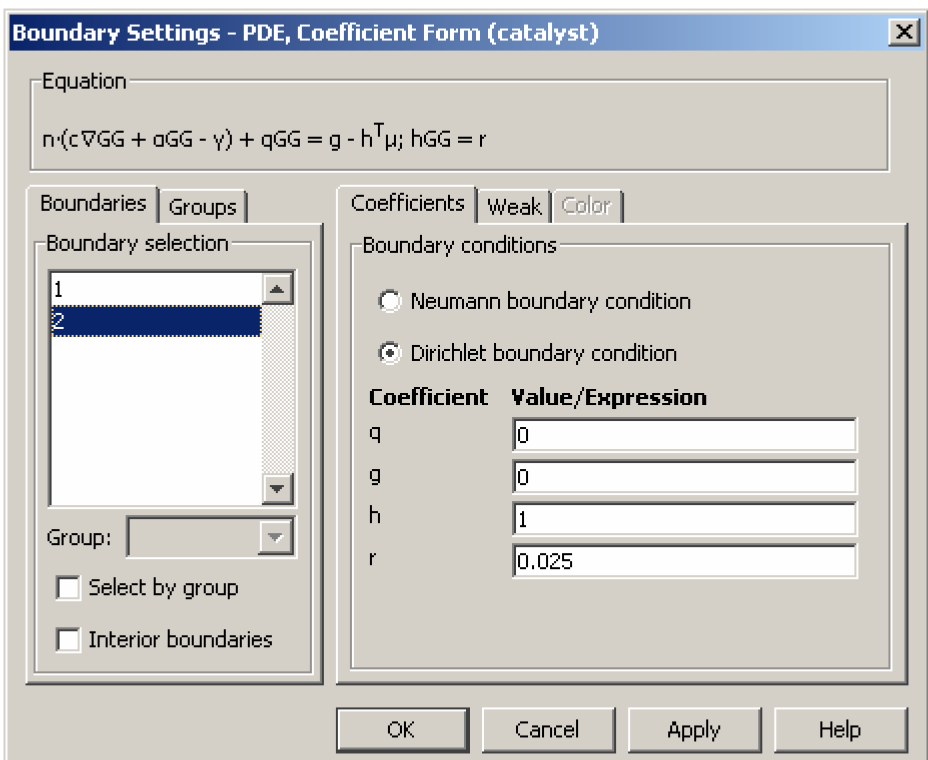
Boundary Conditions

1. From the **Physics** menu choose **Boundary Settings.**
2. In the **Boundary Settngs** dialog box enter the following for boundaries 1 and 2:





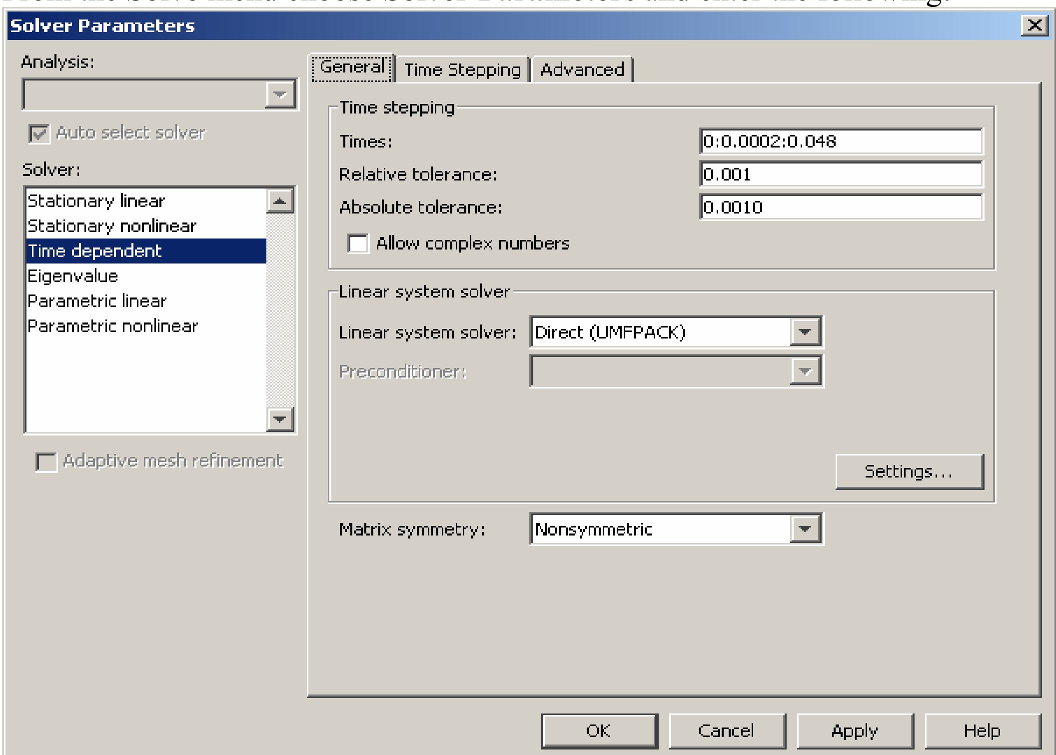
3. Click **OK**.

Mesh Generation

1. Go to the **Mesh** icon on the toolbar and click **initialize mesh** icon.
2. Click on the **refine remesh** icon four times (240 elements).

Computing the Solution

1. From the **Solve** menu choose **Solver Parameters** and enter the following**:**



2. Click **OK**
3. Click **Solve** button on the menu and **Solve Problem** on the dropdown menu

PostProcessing And Visualization

1. Click **Postprocessing** on the menu and the select **Domain Plot Parameters**
2. Select **GG** in **Predefined quantities** and highlight **1** in **subdomain selection.**
3. **Click OK**

The plot of Fig (7) appears. This gives the curves for GG (i. e. Γ) for τ from 0 to 0.048.

Comparison of Solutions

COMSOL Multphysics was originally run with 240 elements. In order to improve the accuracy, the problem is rerun with 61,440 elements. The results are listed in the table of Fig. 8 and illustrated in Fig. 9 and Fig 10.

To obtain the COMSOL values, at selected values of ξ on the COMSOL chart at τ = 0.048 the following procedure is used:

1. Click on **Postprocessing > Data Display > Subdomain**
2. Enter 0.048 in the **Solution at time**.
3. Enter the selected value of **rh** (i. e. ξ).
4. Click **OK**

The value of Γ appears in the lower left part of the screen.

Conclusions

The COMSOL Multiphysics and spreadsheet (analytical) solutions compare quite well using a set of arbitrary parameters. However, a very large number of elements must be used to get reasonably accurate results at small values of ξ using COMSOL.

Eq. (3) appears to be valid for all values of ξ except $\xi = 0$. Values of τ must be greater than 0.

The values of Γ at small values of ξ as determined from Eq (3) at small and large values of τ (steady states) are consistent with the steady state values of at the center (ξ= 0) using Eq. (4).

Papadopoulos (2006) has pointed out that the Laplace inversion of Eq. 32.148 in Spiegel's handbook, 1968 should have a minus sign.

Eq. (26) in Papadopoulos, 2001 also appears to be in error (even with a ' –' sign added in front of the infinite series.) as it fails at $\xi = 1$ though it is numerically correct at other values. The exception, however, is consistent with the inconsistency of Eq. (1) at $\tau = 0$, $\xi = 1$.

References

1. Bartholomew, C. H. and Farrauto, R, J., *Fundamentals of Industrial Catalytic Processes,* 2nd Ed .Wiley Intersciences, 2005

2. Bird, R. B., Stewart, W. E. and Lightfoot, E. N., *Transport Phenomena* John Wiley, New York, 1960.

3. COMSOL Multiphysics, Version 3.2 September 2005a COMSOL. Inc. http://www.comsol.com/

4. COMSOL Multiphysics Modeling Guide, Version 3.2 September 2005b, p 225

5. Papadopoulos, K. D. "Simple Uses of LaPlace Transforms", *Chemical Engineering Education*, **35**, No 4 Fall 2001 p 238

6. Papadopoulos, K. D. Private Communication 1/3/2006.

7. Spiegel, M. R., *Mathematical Handbook of Formulas and Tables*, (Schaum's Outline Series), McGraw-Hill (1968).

```
Function totx(chi, tau, b)

'chi = csi,   tau = tau,   b = beta

Application.Volatile True

Dim n As Integer
Dim Pi, sum, add, b2 As Double
Dim T1, T2, T3 As Double
Dim Q1, Q2 As Double

If chi = 0 Then
  totx = -999
  Exit Function
End If

Pi = 3.14159265
b2 = b * b
sum = 0

For n = 1 To 31000

T1 = Exp(-((n ^ 2 * Pi ^ 2 + b2) * tau))
T2 = (n ^ 2) * (Pi ^ 2) + b2
T3 = ((-1) ^ n) * n * Sin(n * Pi * chi)

add = T1 * T3 / T2
sum = sum + add

If Abs(add) < 1E-25 Then GoTo Skip:

Next n

Skip:

Q1 = Application.Sinh(b * chi) / (chi * Application.Sinh(b))
Q2 = 2 * Pi * sum / chi

totx = Q1 + Q2

End Function
```

Figure 1 VBA Function totx to Evaluate Eq. (3)

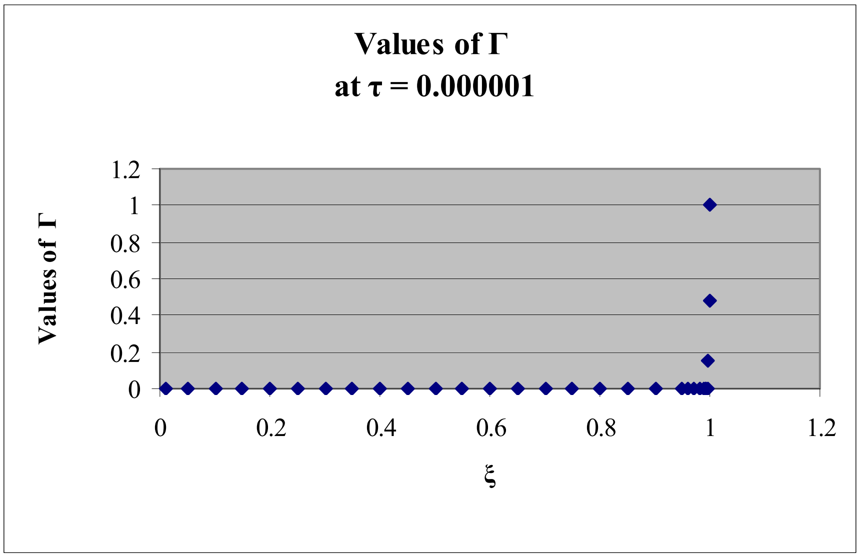


Figure 2 Values of Γ at $\tau = 1.E\text{-}6$ ($\beta = 2.5$)

Porous Catalyst

Parameters

R	0.0005	m
τ	0.048	
t	0.002	s
Ds	6.00E-06	m^2 /s
β * β	6.25	
k_1	150	1/s
C_1	0.015	kg/m^3
β	2.5	
C_2	0.04	kg/m3
ξ	r/R	

Concentration Profile

ξ	$C_{ss1}(\xi)$	$C_{ss2}(\xi)$	C (ξ ,0.048)	Γ (ξ ,048)
0.02	6.2007E-03	1.6535E-02	6.7511E-03	5.5038E-04
0.04	6.2085E-03	1.6556E-02	6.7698E-03	5.6136E-04
0.06	6.2214E-03	1.6590E-02	6.8012E-03	5.7983E-04
0.08	6.2395E-03	1.6639E-02	6.8456E-03	6.0604E-04
0.1	6.2629E-03	1.6701E-02	6.9032E-03	6.4034E-04
0.12	6.2915E-03	1.6777E-02	6.9747E-03	6.8317E-04
0.14	6.3255E-03	1.6868E-02	7.0605E-03	7.3507E-04
0.16	6.3647E-03	1.6973E-02	7.1615E-03	7.9670E-04
0.18	6.4095E-03	1.7092E-02	7.2782E-03	8.6879E-04
0.2	6.4596E-03	1.7226E-02	7.4118E-03	9.5218E-04
0.22	6.5154E-03	1.7374E-02	7.5632E-03	1.0478E-03
0.24	6.5768E-03	1.7538E-02	7.7334E-03	1.1566E-03
0.26	6.6439E-03	1.7717E-02	7.9237E-03	1.2798E-03

Figure 3. Spreadsheet for Concentration and Γ Values

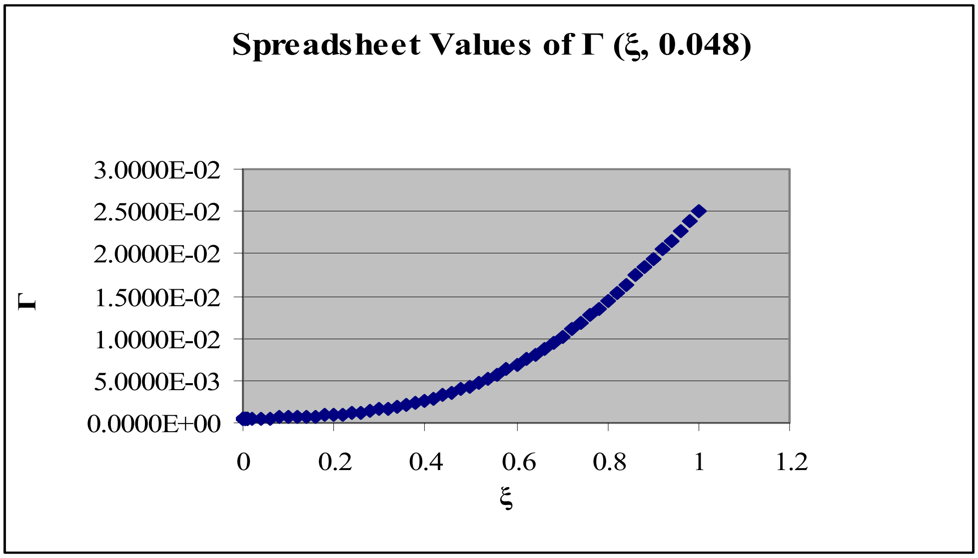


Figure 4 Values of Γ at $\tau = 0.048$ ($\beta = 2.5$)

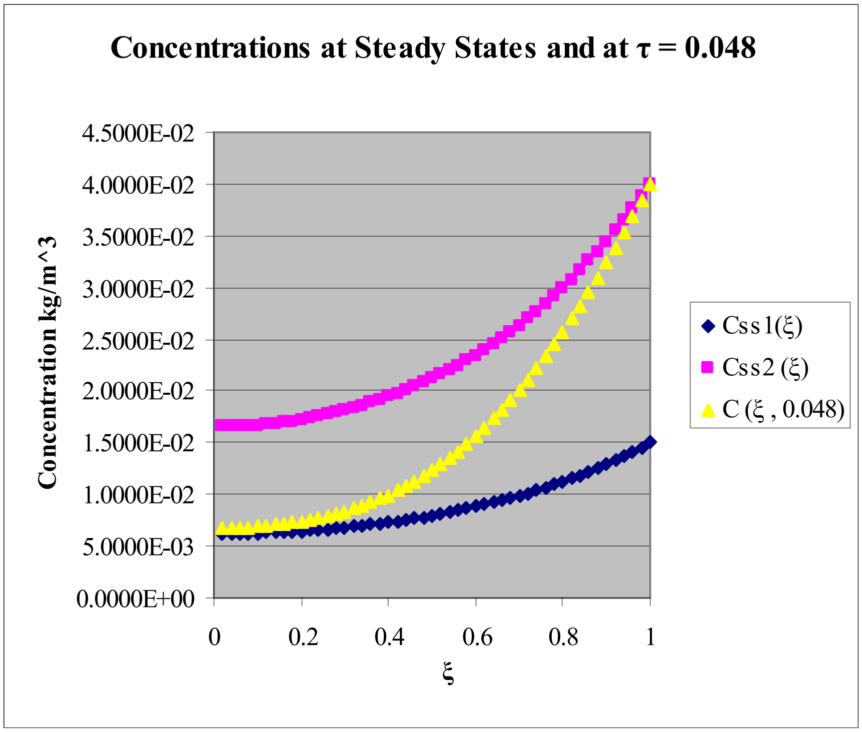


Figure 5. Steady States and Concentration at $\tau = 0.048$ ($\beta = 2.5$)

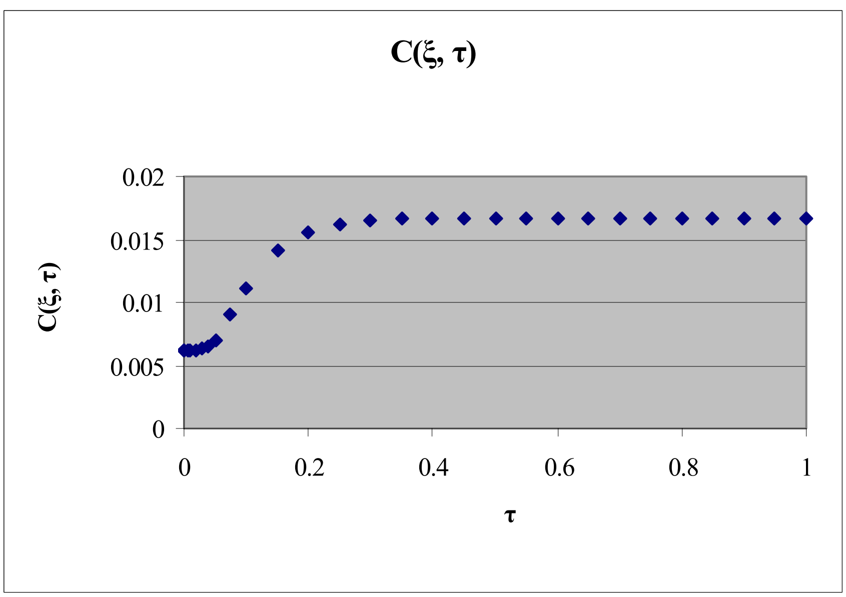


Figure 6 Concentraion vs Time at $\xi = 0.1$ ($\beta = 2.5$)

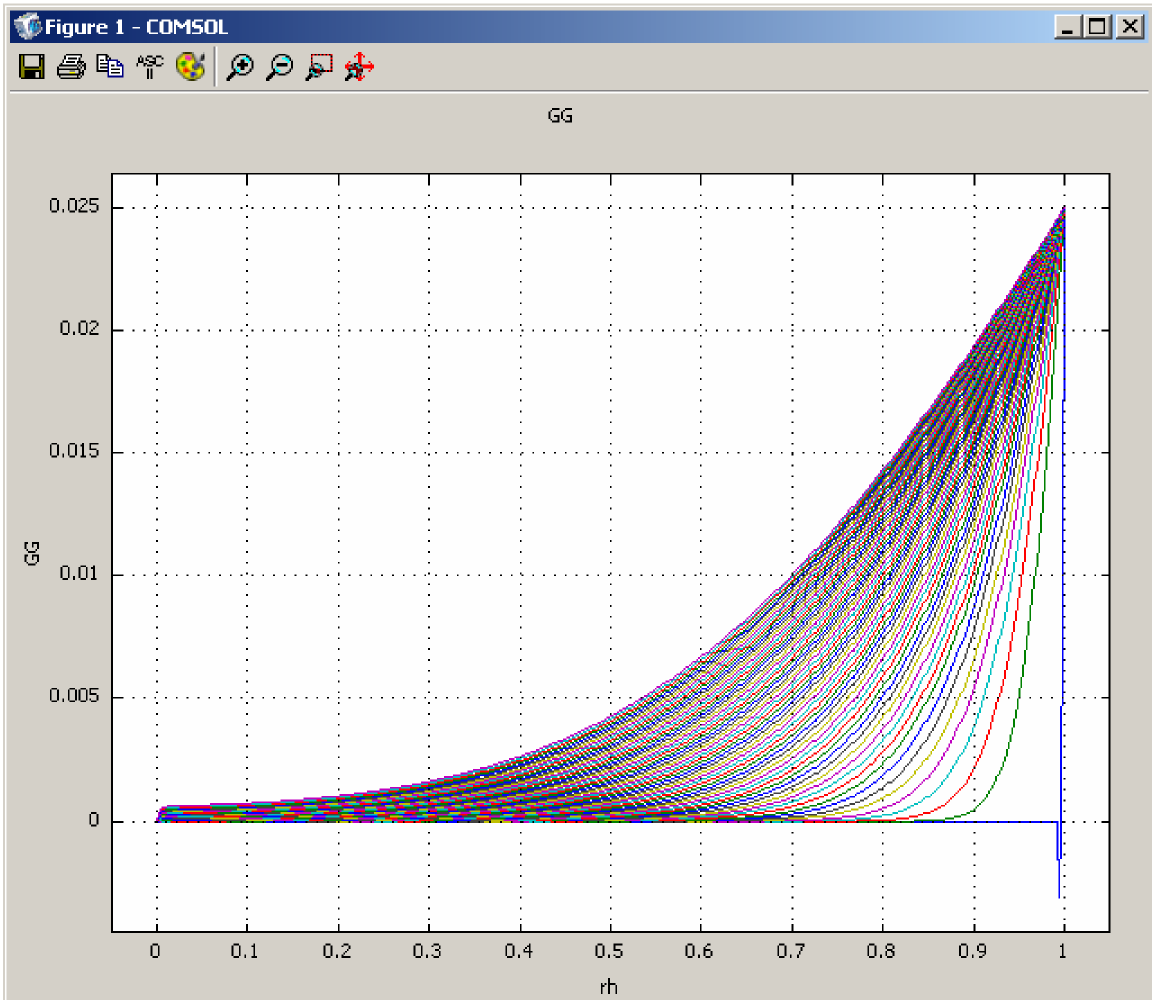


Figure 7. Profiles of GG (i.e Γ) at $\tau = 0$ to 0.048

Catalyst Particle

Parameters

R	0.0005	m
τ	0.048	
t	0.002	s
Ds	6.00E-06	m^2 /s
β^2	6.25	
k_1	150	1/s
C_1	0.015	kg/m^3
β	2.5	
C_2	0.04	kg/m3
ξ	r/R	

ξ	Γ (ξ , 0.048)	Comsol Elements- 240	Comsol Elements- 61440
0.00001	5.46735E-04	3.12553E-06	5.48644E-04
0.0002	5.46735E-04	6.09252E-05	6.71329E-04
0.0004	5.46736E-04		
0.0006	5.46738E-04	1.72762E-04	6.75418E-04
0.0008	5.46741E-04		
0.001	5.46744E-04	2.71248E-04	6.76241E-04
0.0012	5.46748E-04		
0.0014	5.46753E-04		
0.0016	5.46758E-04		
0.0018	5.46764E-04		
0.002	5.46771E-04	4.59051E-04	6.76879E-04
0.0022	5.46779E-04		
0.0024	5.46787E-04		
0.0026	5.46797E-04		
0.0028	5.46806E-04		
0.003	5.46817E-04	5.63409E-04	6.77127E-04
0.0032	5.46828E-04		
0.0034	5.46840E-04		
0.0036	5.46853E-04		
0.0038	5.46866E-04		
0.004	5.46881E-04		
0.0042	5.46896E-04		

0.0044	5.46911E-04		
0.0046	5.46928E-04		
0.0048	5.46945E-04		
0.005	5.46963E-04		
0.0052	5.46981E-04		
0.0054	5.47000E-04		
0.0056	5.47020E-04		
0.0058	5.47041E-04		
0.006	5.47063E-04	6.01133E-04	6.77562E-04
0.0062	5.47085E-04		
0.0064	5.47108E-04		
0.0066	5.47131E-04		
0.0068	5.47156E-04		
0.007	5.47181E-04		
0.0072	5.47207E-04		
0.0074	5.47233E-04		
0.0076	5.47261E-04		
0.0078	5.47289E-04		
0.008	5.47318E-04	6.14669E-04	6.77853E-04
0.0082	5.47347E-04		
0.0084	5.47377E-04		
0.0086	5.47408E-04		
0.0088	5.47440E-04		
0.009	5.47472E-04	6.18608E-04	6.78016E-04
0.0092	5.47505E-04		
0.0094	5.47539E-04		
0.0096	5.47574E-04		
0.0098	5.47609E-04		
0.01	5.47645E-04	6.22154E-04	6.78193E-04
0.0102	5.47682E-04		
0.0104	5.47720E-04		
0.02	5.50379E-04		
0.04	5.61363E-04		
0.06	5.79834E-04	6.77676E-04	7.08597E-04
0.08	6.06043E-04		
0.1	6.40338E-04	7.37186E-04	7.65455E-04
0.12	6.83166E-04		
0.14	7.35072E-04		
0.16	7.96702E-04		
0.18	8.68792E-04		
0.2	9.52177E-04	1.03500E-03	1.05700E-03
0.22	1.04778E-03		
0.24	1.15661E-03		
0.26	1.27977E-03		
0.28	1.41843E-03		
0.3	1.57383E-03	1.62400E-03	1.63600E-03
0.32	1.74727E-03		
0.34	1.94012E-03		
0.36	2.15377E-03		
0.38	2.38966E-03		

0.4	2.64922E-03	2.64700E-03	2.64200E-03
0.42	2.93390E-03		
0.44	3.24513E-03		
0.46	3.58430E-03		
0.48	3.95275E-03		
0.5	4.35176E-03	4.28300E-03	4.25800E-03
0.52	4.78250E-03		
0.54	5.24606E-03		
0.56	5.74336E-03		
0.58	6.27523E-03		
0.6	6.84230E-03	6.71300E-03	6.67200E-03
0.62	7.44505E-03		
0.64	8.08376E-03		
0.66	8.75853E-03		
0.68	9.46926E-03		
0.7	1.02156E-02	1.00580E-02	1.00120E-02
0.72	1.09972E-02		
0.74	1.18132E-02		
0.76	1.26628E-02		
0.78	1.35450E-02		
0.8	1.44585E-02	1.43200E-02	1.42310E-02
0.82	1.54020E-02		
0.84	1.63742E-02		
0.86	1.73735E-02		
0.88	1.83983E-02		
0.9	1.94471E-02	1.93700E-02	1.93490E-02
0.92	2.05184E-02		
0.94	2.16107E-02		
0.96	2.27225E-02	2.26920E-02	2.26830E-02
0.98	2.38526E-02		
1	2.50000E-02	2.50000E-02	2.50000E-02

Figure 8. Table of Γ (ξ, 0.048) from Spreadsheet and COMSOL Multiphysics

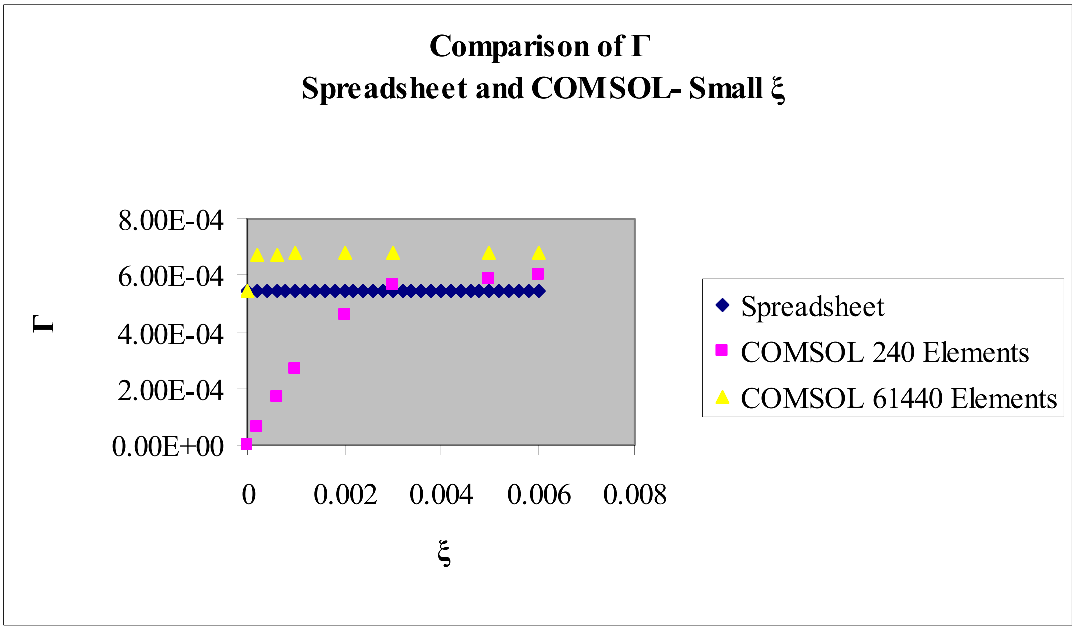


Figure 9. Comparison of Γ : Spreadsheet and COMSOL -: Small ξ

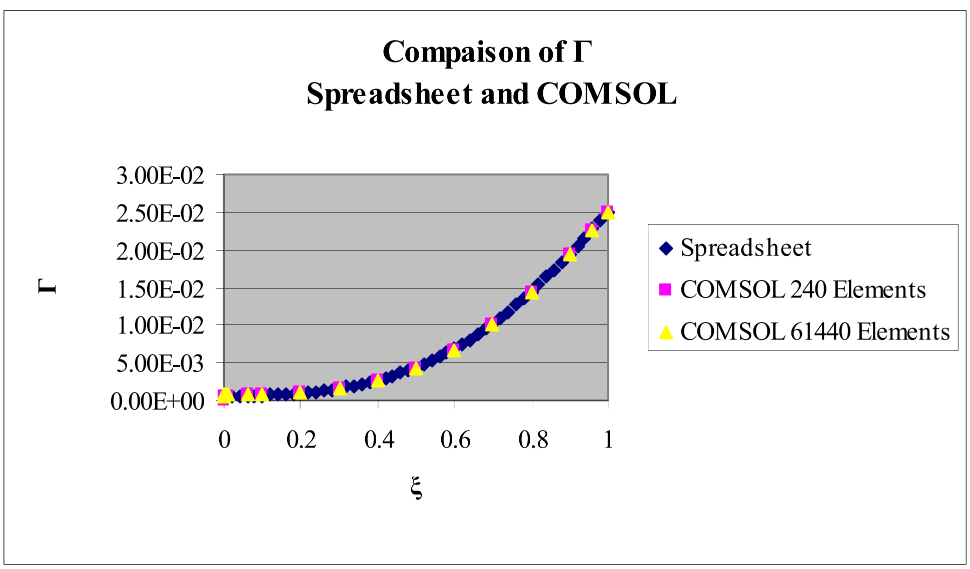


Figure 10. Comparison of Γ: Spreadsheet and COMSOL