

Dynamic Simulation Using COMSOL Multiphysics for Heterogeneous Catalysis at Particle Scale

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Abstract: In this work, dynamic simulation of reaction kinetics at particle scale using COMSOL Multiphysics is carried out. It was observed that the reaction rate and kinetics inside the pores of the catalyst is of higher magnitude as compared to bulk of the liquid. When the reactant mixture is mixed with solid catalyst particles it becomes a uniform particulate-liquid suspension at sufficiently high mixing speed in a batch reactor. Keeping this as hypothesis for the determination of kinetics where each solid catalyst particle is surrounded by reactant mixture which is of equal volume for all the catalyst particles, a dynamic simulation is carried out using COMSOL Multiphysics which has solver for diffusion-reaction equation for both in liquid phase and inside particle. The intrinsic reaction rate constants for bulk liquid phase and the particle are obtained by solving the diffusion-reaction equation and optimization method. The model prediction of overall kinetics is presented.

Keywords: Diffusion; Reaction, Esterification, Kinetics, Simulation; Catalysis

1. Introduction

In solid catalyzed heterogeneous reaction there is a simultaneous reaction and diffusion occurring in the catalyst particles. Such a system is generally difficult to simulate or obtain analytical expression for overall kinetics of reaction conversion. Simulation of reaction diffusion equation was carried out and found to be useful to obtain internal mass transfer coefficients in porous catalysts (Joshi et al, 2009). Simultaneous mass transfer and reaction were also simulated for porous media such as catalytic monoliths (Valdes-Parada et al, 2011).

Esterification of acetic acid (A) with methanol (B) giving rise to methyl acetate (C) and Water (D) using porous solid catalyst particle is one such example as described by Mekala et al. (2013). It was one of the first papers to model

esterification reaction using pore diffusion model. In this work there was an assumption of quasi steady state in simulating the dynamics of concentration profile inside the catalyst particle. The liquid side was assumed to be well stirred and hence a uniform concentration was attributed to all the species. This forms a dirichlet boundary condition instead of flux continuity which is addressed and solved in the present work.

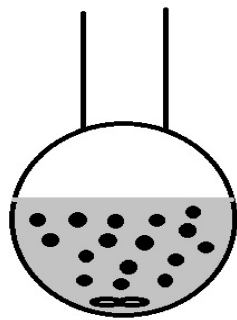
For this liquid state reaction there will be two rate constants one for the forward reaction and another for reverse reaction or it is equivalent to specify forward reaction rate constant k_f and equilibrium constant K_e . It is well established that K_e equals 4.95 for Indion 180, an anionic resin catalyst (Jagadeesh Babu et al., 2011). Other research work also has determined the K_e value as similar (Tsai et al., 2011). The reaction rate expression assuming it as elementary reaction is

$$-r_A = k_f \left(C_A C_B - \frac{C_C C_D}{K_e} \right) \quad (1)$$

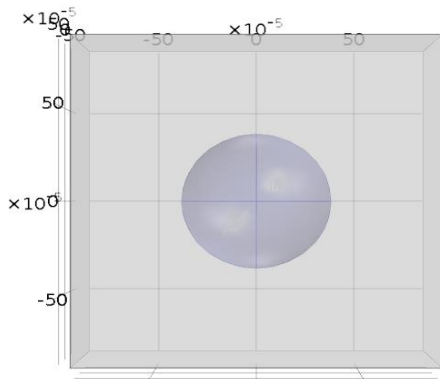
The catalyst particles are spherical in shape and with a diameter in the range of 400 – 1000 μm . The catalyst particles are porous in nature and hence the reactant liquids ingress into the catalyst particles, react and produce products which have to diffuse outward. Due to high catalytic activity inside the pores, the value of k_f will be higher inside the catalyst particle than in the surrounding bulk liquid.

When certain number of catalyst particles are added to the reactant mixture as shown in Figure 1(a), during stirring the particles is uniformly distributed in the liquid and hence each of the particles is surrounded by certain amount of liquid as shown in Figure 1(b).

Therefore to obtain the kinetics of heterogeneous catalytic reaction, the phenomena of reaction and diffusion occurring in this single cell consisting of one spherical catalyst particle surrounded by the liquid is sufficient for simulation purpose. For this purpose it requires the expression for k_{fl} in the liquid phase and k_{f2} in the solid phase. If there is a data of conversion Vs time (X_A Vs t) for a reaction then it was shown for pore diffusion model that the initial rate of conversion dX_A/dt at time 0 is a linear function of catalyst loading w_c (gm of catalyst/cc of liquid) as below (Mekala et al., 2013).



(a)



(b)

Figure 1. (a) Catalyst particles mixed in reactant product solution. (b) Catalyst particle surrounded by liquid.

$$\frac{dX_A}{dt} = \beta_{\text{expt}} w_c + C_{A0} k_{fl} \quad (2)$$

Here C_{A0} is the initial concentration of A. Hence from a plot of dX_A/dt vs w_c will provide the value of k_{fl} from the intercept. Here k_{fl} is the rate constant on the liquid side. The slope β_{expt} has to be related to the rate constant inside the particle k_{f2} by the following relationship (Mekala et al., 2013)

$$\beta_{\text{sim}} = \left(\frac{3D_{A2}}{R_p^2 \rho_p} \right) \left(\frac{\partial C_A}{\partial r} \right)_{r=R_p} \quad (3)$$

where $D_{A2} * \left(\frac{\partial C_A}{\partial r} \right)$ represents the inward flux of A into the catalyst particle at its surface. The concentration profile $C_A(r)$ in Eq. 4 is the solution to the following reaction-diffusion equation inside the catalyst particle.

$$\frac{\partial C_A}{\partial t} = D_{A2} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C_A}{\partial r} \right) - \epsilon [k_{f2} C_A C_B - k_{b2} C_C C_D] \quad (4)$$

It depends on the choice of k_{f2} value which in turn provides such that β_{expt} is matched. Adjust or optimize k_{f2} in Eq. 4 such that β_{sim} from Eq. 3 averaged over first 15 minutes matches with β_{expt} from Eq. 2. And with flux continuity at the surface of the catalyst particle implying that there exists concentration profile of A on both liquid and particle side.

2. Mathematical Model

2.1 Geometry

The basic geometry created in the comsol is a catalyst particle surrounded with certain volume of the reactant mixture. The catalyst particles in reactant-product solution and the associated geometry in comsol is shown in Figure. 2.

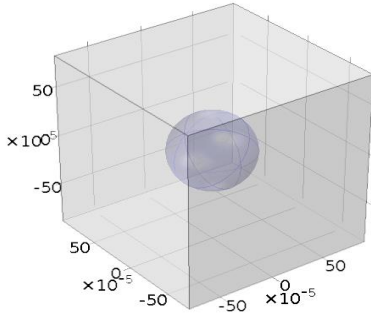


Figure 2. Geometry in COMSOL simulation for the catalyst particle surrounded by a cube of reactant liquid mixture. Units of length is in meters.

2.2 Governing Equations

The mathematical model that is used for this system is distributed parameter model involving time and space as independent variables and concentration or conversion as dependent variable. The generic form of reaction – diffusion equation for species A inside the catalyst particle whose pore volume fraction is equal to ε is as follows

$$\frac{\partial C_A}{\partial t} - D_{A2} \nabla^2 C_A = -\varepsilon k_{f2} \left[C_A C_B - \frac{C_C C_D}{K_e} \right] \quad (5)$$

Where k_{f2} and k_{b2} are the forward and backward rate constants inside the catalyst particle and ε is the available pore volume for the reaction to occur inside the catalyst particle. Since the pore volume is utilized for the reaction this type of model is called as pseudo homogenous model. Also since 1:1 mole ratio of A and B are taken as reactant mixture, it suffices to solve for species A only and rest of them are related through stoichiometry as in Eq. (1). $C_B = C_A$, $C_C = C_{A0} - C_A$ and $C_D = C_{A0} - C_A$. The conversion $X_A = 1 - C_A/C_{A0}$.

The generic form of reaction –diffusion equation in surrounding liquid phase is given as follows

$$\frac{\partial C_A}{\partial t} - D_{A1} \nabla^2 C_A = -k_{f1} \left[C_A C_B - \frac{C_C C_D}{K_e} \right] \quad (6)$$

2.3 Boundary conditions and initial conditions:

At the center of the particle,

$$r = 0, \frac{\partial C_A}{\partial r} = 0, \quad (7)$$

At surface of the particle,

$$r = R_p, C_{A,in} = C_{A,out} \quad (8)$$

$$r=R_p, -D_{A1} \frac{dC_A}{dr} = -D_{A2} \frac{dC_A}{dr} \quad (9)$$

At the faces of the cube, symmetry or no-flux condition is applied

At $t = 0$, $C_A = C_{A0}$, $0 < r < R_p$ and in the bulk liquid (10)

2.4 Simulation Tool

Comsol Multiphysics is finite element based simulation software applicable for many kinds of engineering applications. It consists of different types of modules and selection of each module is application specific. The module we choose for our problem was transport of dilute species. Good solution of partial differential equations can be obtained using comsol and hence it is considered as powerful software package. It can be used in conjunction with MATLAB too.

3. Determination of Rate Constants

3.1. Heterogeneous rate constant

Simulation is done in order to optimize the value of k_{f2} as in Eq. (5). Diffusivities of all species is assumed constant as $D_{A1} = 3 \times 10^{-9} \text{ m}^2/\text{sec}$ in the bulk liquid and $D_{A2} = 1 \times 10^{-9} \text{ m}^2/\text{sec}$ inside the catalyst particle since different diffusivities implies solving equations for all species. Reaction kinetics is used from Mekala et al. 2013. The average concentration of A in the liquid phase is used to evaluate the overall conversion of A. As described earlier, the plot between the error = absolute($\beta_{sim} - \beta_{expt}$) and the guess value of k_{f2} is represented in Figure 3.

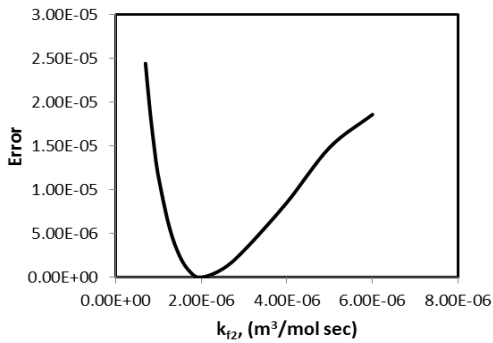


Figure 3. Error plot for evaluating optimum k_{f2} at a temperature of 343.15 K using comsol solution for reaction-diffusion equation.

The values of k_{f1} and k_{f2} obtained are tabulated in table. 1

Table 1. Rate constant values at different temperatures

Temperature (K)	k_{f1} (l/mol min)	k_{f2} (l/molmin)
323.15	0.000414	0.0603
333.15	0.000673	0.0895
343.15	0.001064	0.1298
353.15	0.001638	0.1843

The rate constants k_{f1} and k_{f2} are further fitted to arrhenius rate laws as $k = k_0 \cdot \exp(-E/R \cdot T)$. The linear fit for k_{f2} Vs $1/T$ obtained from model is plotted in Figure 4.

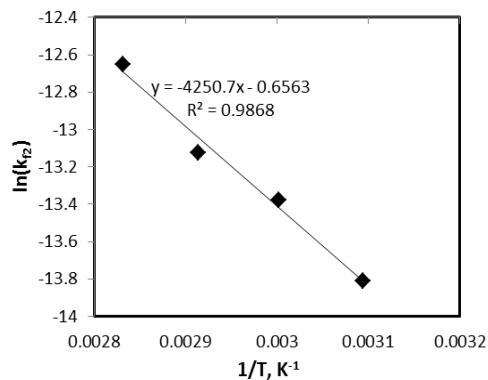


Figure 4. Arrhenius plot for reaction rate constant inside the catalyst pores.

The values of pre-factor k_0 and activation energy E are tabulated for k_{f1} and k_{f2} for the model in table. 2.

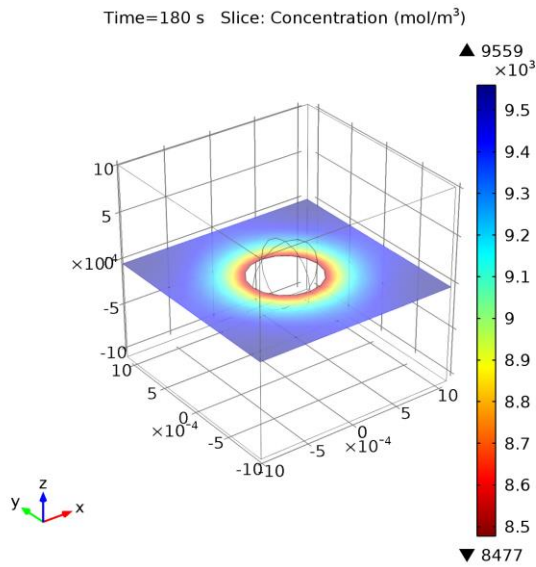
Table 2. k_0 and E values for k_{f1} and k_{f2} for the model

Rate Constant, k_{f1}		Rate Constant, k_{f2}	
Pre Exponential factor, k_0 (l/mol min)	Activation Energy, E (J/mol)	Pre Exponential factor, k_0 (l/mol min)	Activation Energy, E (J/mol)
4465	43507	31126.02	35341.15

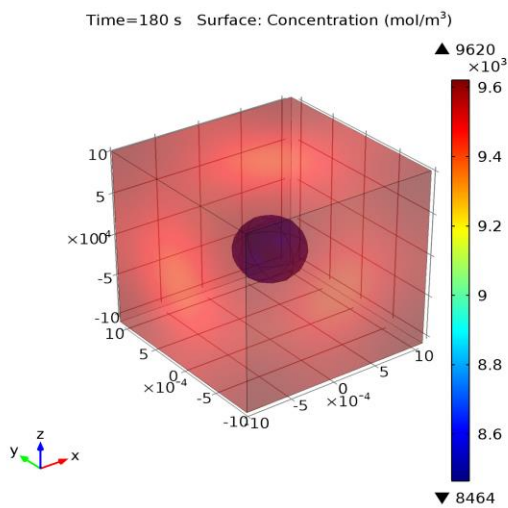
4. Simulation Results

4.1 Concentration distribution inside and outside catalyst particle

The spatial concentration distribution at an instant of time during the dynamic simulation inside the geometry consisting of two domains i.e., one inside the catalyst and the other bulk of the liquid is shown in Figure 5 with the help of slice in the comsol software. As we know the conversion is high in the region inside the catalyst particle as compared to bulk of the liquid, the region inside the particle has lower concentration of the reactant species and in particular that of acetic acid (A). To bring out a clear picture of the concentration distribution in both the domains the concentration profile from one face of the cell to the other face passing through the catalyst at different times is shown in Figure 6.



(a)



(b)

Figure 5. (a) Slice Concentration (b) Spatial concentration distributions inside the catalyst particle and around it in the solution at time $t = 180$ sec, $d_p = 725 \mu\text{m}$, $\text{Temp} = 343.15$ K during dynamic simulation.

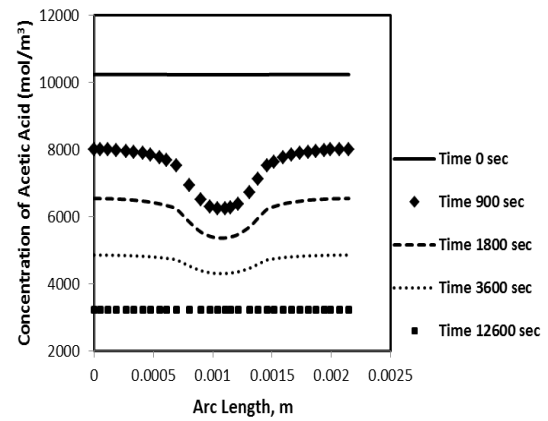


Figure 6. Concentration profiles along an arc length from one face of cell to opposite face passing through the catalyst at different times.

4.2 Effect of particle diameter

The particle diameter effect keeping the same catalyst loading is also simulated. The results were obtained for three different particle sizes for a constant catalyst loading of 0.025 gm/cc and at a temperature of 343.15 K .

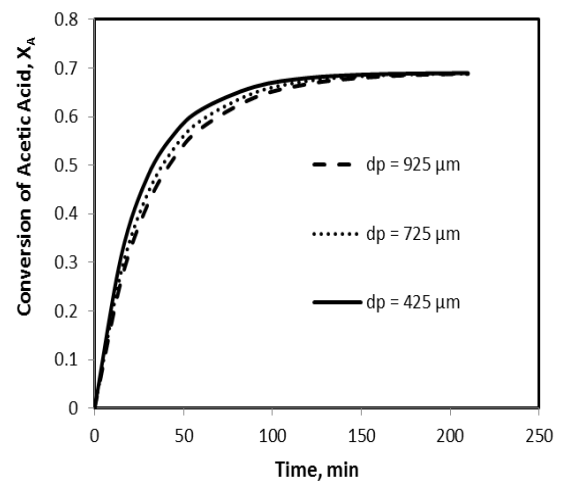


Figure 7. Kinetics of acetic acid conversion for various particle sizes at constant loading of 0.025 g/cc as predicted by the simulation using k_{f1} evaluated with matlab and k_{f2} evaluated with comsol.

Interestingly there is no much variance in the kinetics owing particle size. This must be compared with conventional explanation that reaction rate is proportional to $1/R_p$ i.e., lower the particle size higher is the conversion and it must be attributed when the reaction takes place at the surface of the catalyst in a heterogeneous reaction. In the present case particle pore volume is also utilized and hence the entire volume of catalyst particles is same as long as the catalyst loading is same. But the resultant dependency of the reaction rate over the catalyst particle size can be obtained by solving the reaction – diffusion equation inside the catalyst particle. Figure 7 shows the simulated results of kinetics of acetic acid conversion for different particle sizes and at a constant catalyst loading of 0.025 gm/cc and at a temperature of 343.15 K.

5. Conclusions

A hybrid model for heterogeneous reaction has been developed for carrying out the simulation of the esterification of acetic acid and methanol catalyzed by solids. In this study assumption such as quasi steady state or multi time scale approach as well as well stirred assumption has been relaxed. A more realistic simulation is carried out in which concentration gradients are allowed in the liquid surrounding the catalyst as well. It was observed that pore contribution to overall conversion of acetic acid is higher as compared to bulk of the liquid and is explained with the help of spatial concentration distribution plot as in Figure 6. Further kinetic study was carried out at different intrinsic parameters like particle size.

6. References

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