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Numerical Methods for Mathematical Models of Heterogeneous Catalytic Fixed Bed Chemical Reactors

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Abstract

Mathematical modeling of chemical reactors is of immense interest and of enormous use in the chemical industries. The detailed modeling of heterogeneous catalytic systems is challenging because of the unknown nature of new catalytic material and also the transient behavior of such catalytic systems. The solution of mathematical models can be used to understand the interested physical systems. In addition, the solution can also be used to predict the unknown values which would have been otherwise obtained by conducting the actual experiments. Such solutions of the mathematical models involving ordinary/partial, linear/non-linear, differential/algebraic equations can be determined by using suitable analytical or numerical methods. The present work involves the development of mathematical methods and models to increase the understanding between the model parameters and also to decrease the

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number of laboratory experiments. In view of this, a detailed modeling of heterogeneous catalytic chemical reactor systems has been considered for the present study.

Keywords: heterogeneous reaction, mathematical model, numerical methods, paraffin dehydrogenation, catalytic chemical reaction

1. Introduction

Mathematical modeling of chemical reactors is of immense interest and of enormous use in the chemical industries [1,2,12,21]. Many models that assist the design generally have a detailed physical basis but are simple steady-state models. However they are intended to give accurate descriptions over a wide range of conditions.

Usually the real world system consists of linear / non-linear algebraic / differential / partial steady / unsteady state equations [5-7, 9-14, 17-18, 22]. These equations imitate the actual system and whose solution will give the outputs of such a system when the required input data have been used along with the defining equations. The solutions of such a model can be used in predicting the outputs when some of the input values have been changed without performing the actual experiments [15]. Hence it is obvious that the mathematical models help in favor of economics, man power and the time [4].

In the present work, a detailed modeling of a heterogeneous catalytic chemical reactor system will be considered as it is a challenging task due to the unknown nature of the new catalytic materials and also the transient behavior of such catalytic systems. The physical problem that has been considered for the development of the model is paraffin dehydrogenation which is a catalytic gas-phase reaction. The kinetic parameters have to be extracted by fitting the experimental data to various rate models [16]. The present work involves the development of methods and models to increase the understanding between model parameters and also to decrease the number of laboratory experiments. The effect of more efficient parameter estimation methods should result in faster model development which is required in any process development. Models with diffusion and reaction involve the solution of partial differential equations which considers various catalyst shapes. Apart from developing a model, another important stage to take care of is the procedure to solve the equations, i.e., the mathematical model. Both analytical and the numerical methods can be tried to solve such a system of complicated equations. Some of the numerical methods like Orthogonal Collocation, Runge-Kutta IV order method [1,2], Finite Element Method, Finite Difference Method, Shooting Techniques, Computer Extended Series Method [5,6] can be used to solve the models.

2. Mathematical Formulation

The reactor used for dehydrogenation of paraffins is a fixed bed reactor containing spherical catalyst pellets. The pellet is surrounded by fluid at 2.3 kg/cm^2 pressure and 470ºC temperature containing paraffins stream combined with recycle gas of hydrogen and light paraffins with H_2/HC mole ratio between 3-9. The paraffin stream is a mixture of C_{10}-C_{14} cut. The properties of C_{12} are considered for modeling purpose. The reactions of interest are three major dehydrogenation reactions and one paraffin cracking to light paraffins reaction. Olefins can also crack, but not considered in the present work.

Reactions:

$$P \leftrightarrow O + H_2 \tag{1}$$

$$O \leftrightarrow D + H_2 \tag{2}$$

$$D \rightarrow A + 2H_2 \tag{3}$$

$$P + 3H_2 \rightarrow \text{Lighters} \tag{4}$$

The reaction rate expressions are Langmuir – Hinshelwood – Hougen - Watson type.

Rate equations and kinetic parameters:

$$r_1 = (k_1 p_P - k_{1b} p_O\, p_{H2}) / AP \quad (5)$$

$$r_2 = (k_2 p_O - k_{2b} p_D\, p_{H2}) / AP \quad (6)$$

$$r_3 = k_3 p_D\ / AP \quad (7)$$

$$r_4 = k_4 p_P / P_t \quad (8)$$

$$AP = (p_H + K_2 p_O + K_3 p_D) \quad (9)$$

The rate constants and adsorption constants are assumed to have Arrhenius form.

$$k_1 = 5.825\text{x}10^7 \exp(-19400 / RT)$$

$$k_2 = 4.5\text{x}10^5 \exp(-21000 / RT)$$

$$k_3 = 7.5\text{x}10^6 \exp(-22800 / RT)$$

$$k_4 = 1.74\text{x}10^{18} \exp(-69222 / RT) \quad (10)$$

$$k_{1b} = 0.202 \exp(-9100 / RT)$$

$$k_{2b} = 0.0078\text{x}10^7 \exp(-4600 / RT) \quad (11)$$

$$K_2 = 0.11 \exp(-6800 / RT)$$

$$K_3 = 3.89 \exp(-7200 / RT) \quad (12)$$

The concentration profiles of all the reactants and the products in the pellet are calculated by solving the steady state mass balance equations of the reactants. The product concentrations could simply be calculated by solving their mass balances along with those of the reactants.

$$D_i \frac{1}{r^2} \frac{d}{dr} \{r^2 \frac{dc_i}{dr}\} = -R_i \quad (13)$$

Boundary conditions

$$\frac{dc_i}{dr} = 0\ at\ r = 0 \quad (14)$$

$$\frac{dc_i}{dr} = -k_{mi}(c_{if} - c_i)\ at\ r = R \quad (15)$$

where i = Paraffins, Olefins, Dienes, Aromatics, Hydrogen and Lighters. The mass transfer coefficients are calculated from literature [3, 8]. The effective diffusivity for transport inside the catalyst are also determined from literature [19, 20]. Heat of reaction values are presented in Table 1.

Parameter	Value	Units
ΔH_{R1}	31100	cal / mol
ΔH_{R2}	15191	cal / mol
ΔH_{R3}	30528.7	cal / mol
ΔH_{R4}	-11032	cal / mol

Table 1: Heat of reaction

The numerical solution of these problems is challenging for two reasons. Firstly, steep concentration profiles often occur for realistic parameter values, and these profiles have to be computed accurately. It is not unusual for species concentrations to change by 10 orders of magnitude within the pellet for realistic reaction and diffusion rates. Secondly, the problem is a boundary-value problem because the boundary conditions are provided at the center and at the exterior surface of the pellet. Boundary value problems (BVPs) are generally much more difficult to solve than the initial-value problems (IVPs). The model is solved using the Orthogonal Collocation method [23]. The reactant and the main product concentration profiles are shown in Figures 1-2. Paraffin concentration reached very low value within the pellet. External mass transfer effect is not noticeable.

Figure 2 shows the concentrations of olefins and dienes. Both olefins and dienes concentrations increased near the pellet surface initially and then decreased. It is due to the first dehydrogenation reaction of paraffins to olefins and then the second dehydrogenation reaction of olefins to dienes. Similarly, dienes concentration increased initially near the surface and then decreased indicating the secondary dehydrogenation reaction of dienes to form aromatics. Figures 1-2 show that the reaction is completed at pellet radius of 0.015 cm and remained constant thereafter.

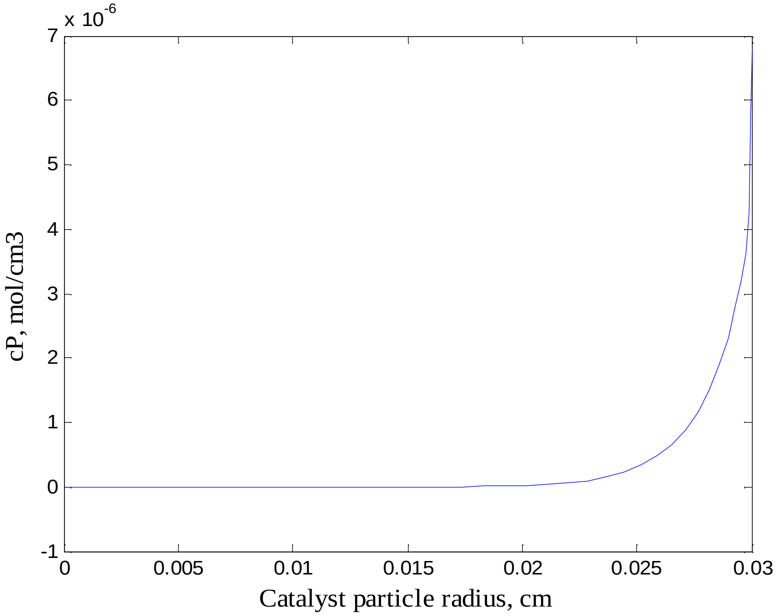

Figure 1: Concentration profile of paraffins

Fixed Bed Reactor Design

With detailed understanding of the behavior of a single catalyst particle, it is possible to solve the design equations of the fixed bed reactor packed with bed of these catalyst particles. In the fixed bed reactor, it is required to keep track of two phases. The fluid-phase streams through the bed and transports the reactants and the products through the reactor. The reaction-diffusion processes take place in the solid-phase catalyst particles. The two phases communicate to each other by exchanging mass and energy at the catalyst particle exterior surfaces.

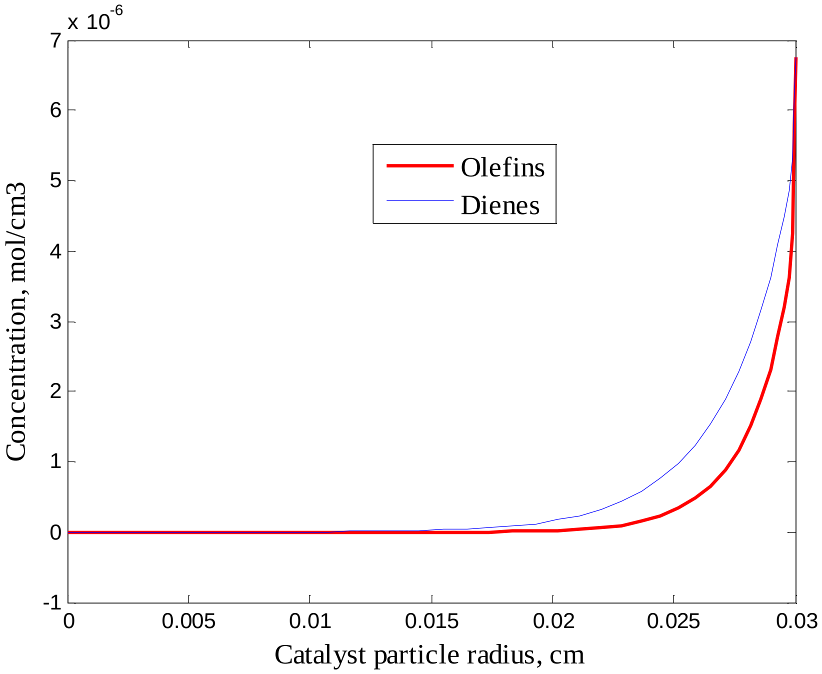

Figure 2: Concentration profiles of olefins and dienes

Coupling the Catalyst and the Fluid

The model assumptions are:

- Uniform catalyst pellet exterior
- Particles are small compared to the length of the reactor
- Plug flow
- No radial profiles
- Axial diffusion is neglected
- Steady state

Fluid phase

The differential mass and energy balance equations in the fluid phase are as follows:

$$\frac{dN_i}{dV} = R_i \tag{16}$$

Component mass balance equations for Fluid Phase:

$$\frac{dN_P}{dV} = -a_k D_{\mathrm{eP}} \left(\frac{dC_{P,k}}{dr}\right)_{dp/2} \tag{17}$$

$$\frac{dN_O}{dV} = -a_k D_{\mathrm{eO}} \left(\frac{dC_{O,k}}{dr}\right)_{dp/2} \tag{18}$$

$$\frac{dN_D}{dV} = -a_k D_{\mathrm{eD}} \left(\frac{dC_{D,k}}{dr}\right)_{dp/2} \tag{19}$$

$$\frac{dN_H}{dV} = -a_k D_{\mathrm{eH}} \left(\frac{dC_{H,k}}{dr}\right)_{dp/2} \tag{20}$$

$$\frac{dN_A}{dV} = -a_k D_{\mathrm{eA}} \left(\frac{dC_{A,k}}{dr}\right)_{dp/2} \tag{21}$$

$$\frac{dN_{LA}}{dV} = -a_k D_{\mathrm{eLA}} \left(\frac{dC_{LA,k}}{dr}\right)_{dp/2} \tag{22}$$

$$Q_{\rho} C_p \frac{dT}{dV} = \sum_{i=1}^{4} \Delta H_{Ri} r_i \tag{23}$$

The fluid-phase boundary conditions are provided by the known feed conditions at the tube entrance z =0.

$$N_i = N_{if}; C_P = C_P^0; C_O = C_O^0; C_D = C_D^0; C_A = C_A^0; C_H = C_H^0; C_{LA} = C_{LA}^0; T = T_{in} \tag{24}$$

where i = P, O, D, A, H, LA.

Solid Phase

The concentrations of all the species have been determined inside the catalyst particle. Temperature and pressure effects inside the catalyst particle can be neglected. The continuity equations for all the species in the catalyst particle are given as follows:

$$D_i \frac{1}{r^2}\frac{d}{dr}\{r^2 \frac{dc_i}{dr}\} = -R_i \tag{25}$$

$$\frac{d^2C_{P,k}}{dr^2} + \frac{2}{r}\frac{dC_{P,k}}{dr} = \frac{1}{D_{eP}}(r_1 + r_4) \tag{26}$$

$$\frac{d^2C_{O,k}}{dr^2} + \frac{2}{r}\frac{dC_{O,k}}{dr} = \frac{1}{D_{eO}}(-r_1 + r_2) \tag{27}$$

$$\frac{d^2C_{D,k}}{dr^2} + \frac{2}{r}\frac{dC_{D,k}}{dr} = \frac{1}{D_{eD}}(-r_2 + r_3) \tag{28}$$

$$\frac{d^2C_{H,k}}{dr^2} + \frac{2}{r}\frac{dC_{H,k}}{dr} = \frac{1}{D_{eH}}(-r_1 - r_2 - 2r_3 + 3r_4) \tag{29}$$

$$\frac{d^2C_{A,k}}{dr^2} + \frac{2}{r}\frac{dC_{A,k}}{dr} = \frac{1}{D_{eA}}(-r_3) \tag{30}$$

$$\frac{d^2C_{LA,k}}{dr^2} + \frac{2}{r}\frac{dC_{LA,k}}{dr} = \frac{1}{D_{eLA}}\left(-\frac{12}{15}r_4\right) \tag{31}$$

$$R_P = -r_1 - r_4 \tag{32}$$

$$R_O = r_1 - r_2 \tag{33}$$

$$R_D = r_2 - r_3 \tag{34}$$

$$R_A = r_3 \tag{35}$$

$$R_H = r_1 + r_2 + 2r_3 - 3r_4 \tag{36}$$

$$R_{LA} = \frac{12}{15}r_4 \tag{37}$$

Boundary conditions

The boundary conditions are provided by the mass-transfer and the heat transfer rates at the pellet exterior surface, and the zero slope conditions at the centre of the pellet.

$$\frac{dc_i}{dr} = 0 \text{ at } r = 0$$

$$\left(\frac{dc_{P,k}}{dr}\right) = \left(\frac{dc_{O,k}}{dr}\right) = \left(\frac{dc_{D,k}}{dr}\right) = \left(\frac{dc_{A,k}}{dr}\right) = \left(\frac{dc_{LA,k}}{dr}\right) = 0 \text{ at } r = 0 \text{ and } \forall\, z \quad (38)$$

$$D_i \frac{dc_i}{dr} = -k_{mi}\left(c_{if} - c_i\right) \; at\; r = R \quad (39)$$

Coupling equations

Fluid and solid phase equations are coupled by equating the production rate R_j experienced by the fluid phase to the production rate inside the particles, which is where the reaction takes place. These expressions are given below:

$$R_j = -(1 - \varepsilon_b) \frac{S_P}{V_P} D_j \left(\frac{dC_j}{dr}\right)_{r=R} \quad (40)$$

The bed porosity is required to convert the rate per volume of particle to the rate per volume of reactor. The bed porosity or void fraction, ε_b, is defined as the volume of voids per volume of reactor. The volume of catalyst per volume of reactor is therefore

$(1 - \varepsilon_b)$. This information can be presented in a number of equivalent ways. The density of the pellet, ρ_p and the density of the bed, ρ_B can easily be measured. From the definition of bed porosity:

$$\rho_B = (1 - \varepsilon_b)\, \rho_P \quad (41)$$

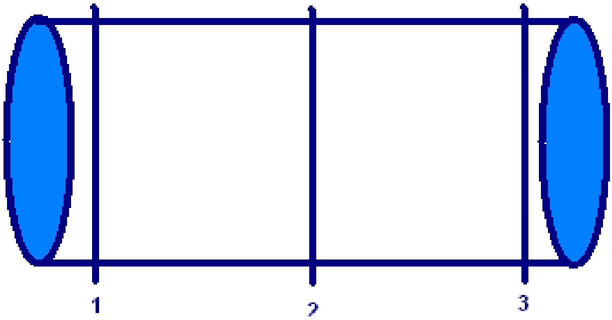

Figure 3: Reactor positions for pellet profiles

The void fraction can be represented by the following equation:

$$\varepsilon_b = (1 - \rho_B / \rho_P) \qquad (42)$$

Figure 3 shows the reactor positions where the pellet concentration profiles are plotted.

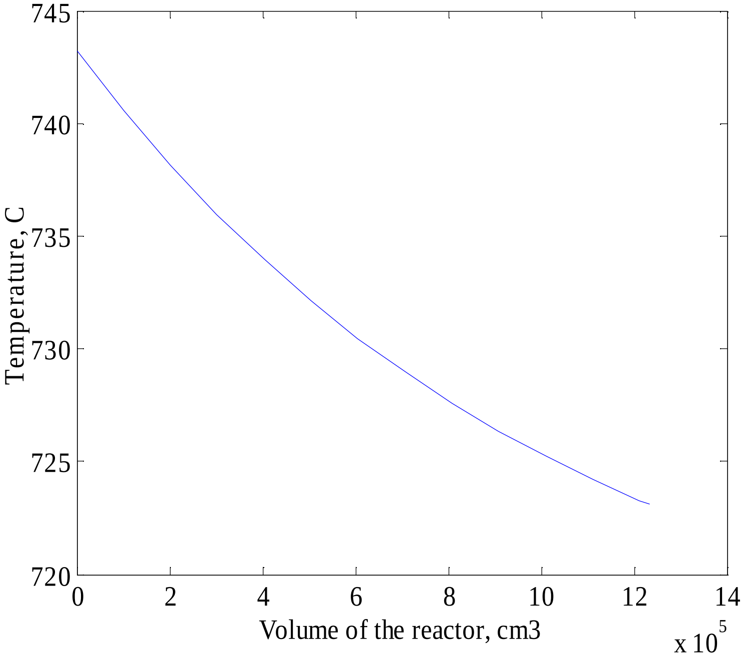

Figure 4: Temperature profile

Orthogonal Collocation method

The orthogonal collocation method is a useful method for problems whose solution has steep gradients and the method can be applied to time-dependent problems, too [23]. This method is used to obtain approximate solutions to the differential equations modeling chemical reactors and etc. An approximate solution to an ordinary differential equation on an interval is an element from some finite-dimensional space, namely the collocation space. This element should satisfy the original ordinary differential equations on an appropriate finite set of points, namely the set of collocation points. It should also satisfy the initial and the boundary conditions specified along with the ordinary differential equation. The ability of the method depends on the selection of the collocation points. The results are not satisfactory when the points are selected at the equal distance. If the roots of an appropriate orthogonal polynomial are considered for the location of the collocation points, the results are better and hence the name orthogonal collocation.

3. Results and Discussions

The model first solves the continuity equations in the pellet at the entrance of the reactor tube with inlet feed concentrations as initial guess values and then goes down the bed. The program stops when the paraffin conversion reaches the desired value and/or the pressure reaches the upper limit. Figure 4 shows the temperature profile in the reactor. Dehydrogenation reactions are endothermic and around 17ºC temperature drop is obtained from the model. The fluid phase concentrations of paraffins, olefins and dienes vs. reactor volume are shown in Figures 5. Figures 6-7 show the concentration profiles of paraffins and olefins respectively in the pellet at three positions of the reactor. The three positions include the reactor inlet, a middle position and the outlet. The model converged at 50 collocation points very smoothly and beautifully as can be observed from the plots. Since the reactants are consumed in the pore reaction, the concentration of reactant decreases from the outside towards the inside of the pores (Fig. 1). Products flow out of the pellet. The movement of the components by diffusion through the pores and the return of the reaction products by the same path but in the reverse direction constitute a mass transfer resistance to the reaction. The reaction is complete at 0.02 cm of catalyst size from the surface. The concentrations of reactants reached a very low value in the pellet itself. The consumption rate is high compared to the diffusion rate. The profiles become flatter near the exit of the reactor. It can be numerically challenging to calculate the rapid changes and the profiles inside the pellet. All of the reaction is occurring in 50% of the size from the pellet exterior. Number of collocation points is changed to vary the numerical approximation in the pellet profile to ensure convergence in the fluid profiles.

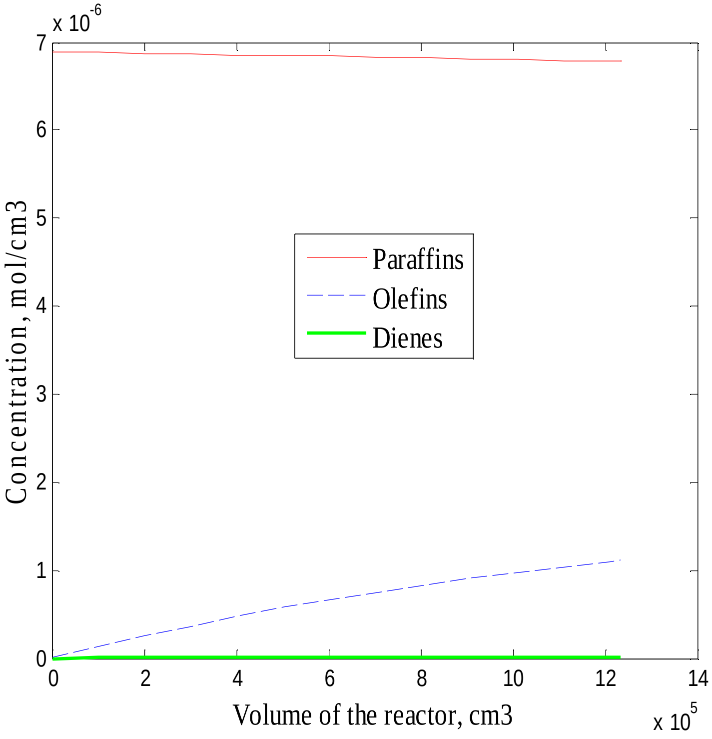

Figure 5: Concentration profiles of paraffins, olefins and dienes

4. Conclusion

The complex reaction – diffusion problem for a system of multiple reactions inside the pellet coupled to the mass and energy balance of the fluid phase has been numerically solved. Orthogonal Collocation method has been used to solve the particle equations. The fluid phase equations have been solved by the Runge-kutta method. The model predicted paraffin conversion, olefins selectivity, yields and the corresponding reactor volume required. The calculated values matched well with that of the actual values.

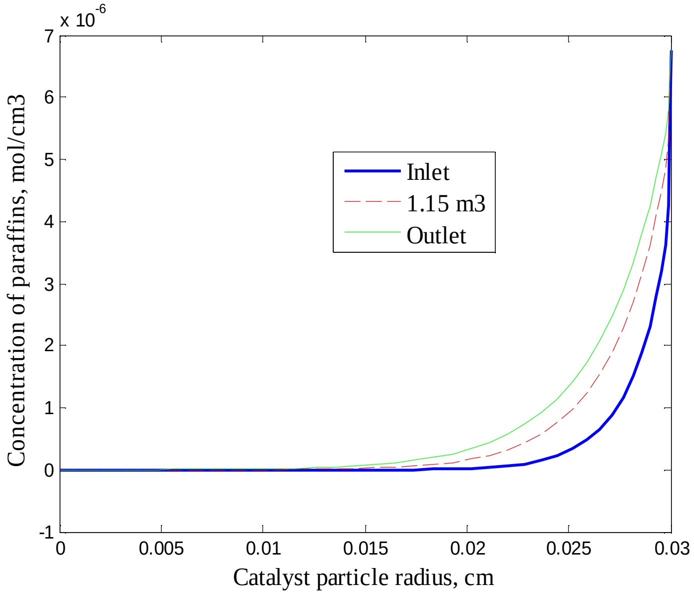

Figure 6: Pellet paraffin profiles at three reactor positions

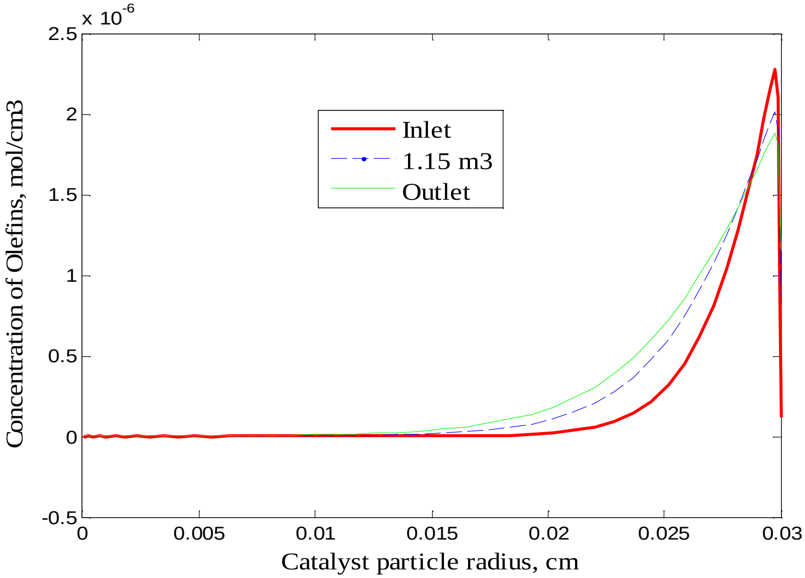

Figure 7: Pellet olefins profiles at several reactor positions

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