

Modeling Of Carbon Deposit From Methane Gas On Zeolite Y Catalyst Activity In A Packed Bed Reactor

Ibrahim, S., Onifade, K.R., Kovo, A.S., Abdulkadir, M. and Otaru, A.J.

¹(Ovecon Engineering and Consultancy, P.O. Box 1730, Zaria, Nigeria)

^{2,3,4&5}(Department of Chemical Engineering, Federal University of Technology, PMB 065, Gidan Kwanu, Minna, Niger State, Nigeria).

ABSTRACT: The purpose of this research work is to study the effects of carbon deposit from methane gas on Zeolite Y catalyst activity in a packed bed reactor. Computational fluid dynamic model was carried with the aid of chosen geometry, governing equation, properties of the fluid and time step. Result shows that increase in time from 0 to 1000s yielded an increase in the formation of hydrogen from 0 to 42mol/dm³, increased carbon from 0 to 21mol/dm³, and decreased methane concentration from 50 to 29mol/dm³. It shows that methane decomposition is taking place. the carbon deposition on catalyst is faster from time 0 to 400 s and above 500 s carbon deposition is lower. This shows that the variation of catalyst activity dropped on carbon deposition. The concentration of carbon and hydrogen formed is less when catalyst deactivation is taking place compared to when catalyst deactivation is not taking place.

Keywords: Carbon, Deposit, Methane, Reactor and Zeolite Y.

I. Introduction

The recent development in petroleum refining technology has brought the hydro processing reaction to a level of economic importance matching cracking and reforming (Wilson, 1997). Carbon deposition onto the surface of solid catalysts is commonly observed in hydrocarbon processing. Carbon deposits can affect both the activity of catalysts as well as the flow of gas through a catalyst bed. These effects of carbon deposit vary from one type of catalyst to another (Szepe and Levenspiel, 1971). Comsol, 2008 investigated the effect of carbon deposit has on Ni/Al₂O₃ catalyst due to methane decomposition in a packed bed reactor and concluded that carbon deposit affect Ni/Al₂O₃ catalyst activity gas flow through the packed bed.

Catalyst developed for fluid catalytic cracking as stated by (Gates et al 1979) includes zeolite. Commercial FCC catalyst consist of zeolite y and dispersed in a porous amorphous matrix comprised of clay and are held together by binder. The zeolite y and active alumina dispersed in a porous amorphous matrix comprised of clay catalyst are in most general use today because they have proven to be highly selective, easy to regenerate, and resistant to poisons.

Carbon deposition onto the surface of solid catalysts is commonly observed in hydrocarbon processing. Carbon deposits can affect both the activity of catalysts as well as the flow of gas through a catalyst bed (Sharif et al., 2004). Catalyst loss its activity with time-on-stream that is deactivation is one of the major problems related to the operation of heterogeneous catalysis. The deactivation process occur both chemical and physical nature simultaneously with the main reaction were commonly divided in to four classes poisoning, coking, fouling and loss of active element. Deactivation is inevitable but can be slowed or prevented and some of its consequences can be avoided (Corolla et al., 1997).

In Nigeria, the Petroleum Technology Development Fund (PTDF) setup a chair in Ahmadu Bello University Zaria to produce indigenous catalyst (Zeolite Y) in other to promote local content. In view of this it is necessary to investigate how carbon deposits can affect both the activity of catalysts as well as the flow of gas through a catalyst bed.

Computational fluid dynamic (CFD) is a reliable tool when modeling and stimulating flow and heat transfer phenomena for designing process equipment without performing an actual experiment (Ali and Rohani, 1997). In a last decade, CFD has been considered as a powerful tool to help chemical engineering development. Comsol multiphysics is a CFD software that is based on novel approach to computer aided modeling and optimizing mixing, Modeling analysis involving Lagrangian and Eulerian analysis for relative fluid stretching and energy dissipation concepts for laminar and turbulent flows. One of the important advantages of using comsol multiphysics in engineering application is the availability of the built in function in each application mode. In addition, visualization of concentration profile of reactant and products within the reactor is possible. Finally, with the above stated reasons, the use of CFD modeling to investigate how carbon deposits can affect both the activity of catalysts as well as the flow of gas through a catalyst bed is inevitable.

A CFD model will be developed to investigate the effect of carbon deposition on FCC catalyst in the FCC reactor. In the first model, the influence of carbon deposition on catalyst activity will be considered. In the second model, the effect that the carbon deposits have in fluid flow will also be investigated.

II. Research Methodology

This research, model and simulates carbon deposition on zeolite Y catalyst by catalytic decomposition of methane to hydrogen in a FCC reactor using Computational Fluid Dynamics (CFD). Two models were developed in this study. In the first model, the influence of carbon deposition on catalyst activity was considered. In the second model, the effect that the carbon deposits have on the fluid flow was investigated. The second simulation takes place in comsol multiphysics, taking both time and space dependencies into account.

The Fluid Catalytic Packed Bed Reactor

The model consists of the FCC reactor packed with zeolite Y catalyst where methane gas is charged into it and it decomposed to carbon and hydrogen by catalytic cracking as shown in the Figure 1. The coloured region is the zeolite packed region of the reactor while the plain region is the region gas entry and exit from the reactor. A flow reactor is set up in 2D. Methane enters from the left and reacts in the porous catalytic bed in the mid-section of the geometry. The model is geometry modeling which is applicable to CFD and is represented as Figure 1

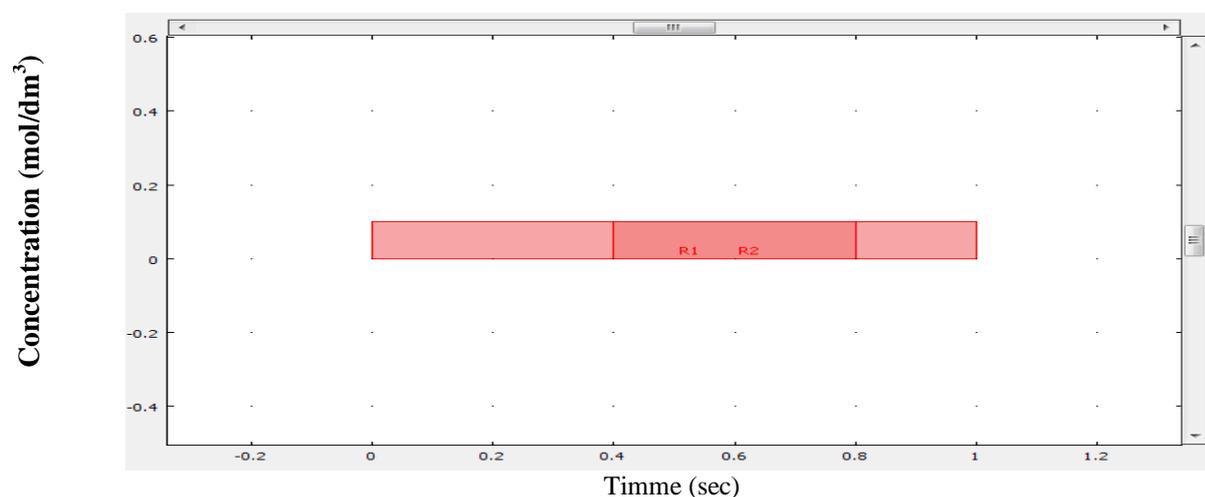


Figure 1: FCC Model showing the entering and exiting gas and the zeolite packed region of the reactor.

Problem Statement

Fifty mol/m³ of methane gas is charged into an FCC reactor where it is flowing through a packed bed of zeolite Y catalyst at temperature of 727°C. The methane is cracked on the zeolite catalyst producing carbon deposit on the catalyst surface and hydrogen gas. The hydrogen gas exit the contacting bed at temperature of 727°C. Determine the following:

- The effect of carbon deposition on catalyst activity.
- The effect that the carbon deposit have on fluid flow taking both space and time dependencies into account.

Geometry

The work models of carbon deposit on the surface of zeolite Y catalytic due to decomposition of methane to carbon and hydrogen gas in packed bed reactor. The packed bed fluid catalytic reactor is represented by a 2D geometry as seen in Figure 2.



Figure 2: The Packed Bed Fluid Catalytic Reactor Model

Axis and Grid Settings

Table 1 Coordinate for drawing the geometry of the FCC packed bed reactor in 2D

Size	Position		
Width	1	X	0
Height	0.1	Y	0

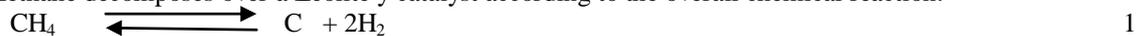
Table 2 Coordinate for drawing the geometry of the packed bed region of the FCC packed bed reactor in 2D

Size	Position		
Width	0.4	x	0.4
Height	0.1	y	0

The coordinate for drawing the geometry of the FCC packed bed reactor and the catalyst packed region of the reactor in 2D is shown in Table 1 and Table 2.

Chemistry

Methane decomposes over a Zeolite y catalyst according to the overall chemical reaction:



The following reaction rate expression has been reported in the literature (Shariff et-al, 2004): relating the rate of reaction and the concentration of various species is

$$r = k \cdot \frac{p_{\text{CH}_4} - \frac{p_{\text{H}_2}^2}{K_p}}{(1 + k_H \sqrt{p_{\text{H}_2}})^2} \tag{2}$$

Where

$$k = 2.31 * 10^{-5} * \exp\left(20.492 - \frac{104200 \text{ J/mol}}{R_g T}\right) \frac{\text{mol}}{\text{m}^3 \cdot \text{s} \cdot \text{bar}}$$

$$k_H = \exp\left(\frac{163200 \text{ J/mol}}{R_g T} - 22.426\right) (\text{bar})^{-1/2}$$

And

$$K_p = 5.088 * 10^5 * \exp\left(-\frac{91200 \text{ J/mol}}{R_g T}\right) \text{ bar}$$

Reactor model

The first model in Comsol Reaction Engineering Lab .was set up This model treats the isothermal decomposition of methane (Equation 1) in a perfectly mixed reactor with constant volume. The species mass balances are summarized by

$$\frac{dc_i}{dt} = R_i \tag{3}$$

The rate term, R_i (mol/(m³·s)), takes into account the reaction stoichiometry, v_i , the reaction rate, r (mol/(m³·s)), and the catalyst activity, a :

$$R_i = V_i r_a \tag{4}$$

The mass balances of the reacting species are then

$$\frac{dc_{\text{CH}_4}}{dt} = -r_a \tag{5}$$

$$\frac{dc_c}{dt} = r_a \tag{6}$$

$$\frac{dc_{H2}}{dt} = 2r_a \tag{7}$$

The time dependence of the catalytic activity is expressed by the ODE

$$p = R_g T(C_{CH4} + C_{H2}) \tag{8}$$

Where

$$k_a = \exp\left(\frac{135600J}{mol} - 32.007\right) \left(\frac{m^3}{mol}\right)^3 \cdot s$$

Solving the mass balances provides the evolution of the species concentrations over time. The fact that carbon is in the solid phase is taken into account by removing its effect on gas phase physical properties. The pressure in the reactor is a function of only the methane and hydrogen concentrations:

$$p = R_g T(C_{CH4} + C_{H2}) \tag{9}$$

Space- and time-dependent Model

The second model is solved in comsol multiphysics and takes both fluid flow and the chemical reaction into account.

The flow reactor is set up in 2D, as illustrated below:

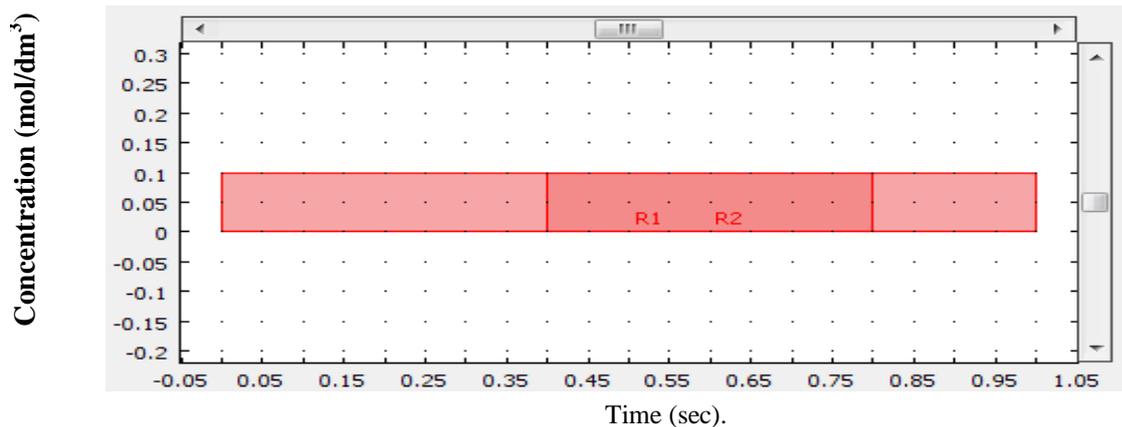


Figure 4: A flow reactor is set up in 2D. Methane enters from the left and reacts in the porous catalytic bed in the mid-section of the geometry.

Methane first flows through a free section of the reactor, and then encounters a porous catalytic bed where the decomposition reaction takes place.

Momentum Balances

The flow in the free channel section is described by the Navier-Stokes equations:

$$\rho \frac{\partial \mathbf{u}}{\partial t} + \nabla \cdot [-\eta(\nabla \mathbf{u} + (\nabla \mathbf{u})^T) + \rho \mathbf{I}] = \rho(\mathbf{u} \cdot \nabla) \mathbf{u}$$

$$\nabla \cdot \mathbf{u} = 0 \tag{10}$$

Where ρ denotes density (kg/m^3), \mathbf{u} represents the velocity (m/s), η is the dynamic viscosity (Pa·s), and p refers to the pressure (Pa). In the porous domain, the Brinkman equations govern the flow:

$$\frac{\rho}{\epsilon_p} \frac{\partial \mathbf{u}}{\partial t} + \nabla \cdot \left[\frac{\eta}{\epsilon_p} (\nabla \mathbf{u} + (\nabla \mathbf{u})^T) + \rho \mathbf{I} \right] = -\frac{\eta}{k} \mathbf{u} \tag{11}$$

Where ϵ_p is the porosity and k denotes permeability (m^2) of the porous medium. As shown in Equation 10 and 11, the momentum-balance equations are closely related. The term on the right-hand side of the Navier-Stokes

formulation corresponds to momentum transported by convection in free flow. In the Brinkman formulation, this term is replaced by a contribution associated with the drag force experienced by the fluid as it flows through a porous medium. Comsol multiphysics automatically combine free and porous-media flow to solve the equations simultaneously.

The boundary conditions for the flow are:

$$u \cdot n = u_o \quad \text{inlet}$$

$$u = 0 \quad \text{walls}$$

$$p = 0 \quad \text{outlet} \tag{12}$$

The boundary condition for the inlet condition shows where the fluid enters the packed bed reactor and all other point are walls.

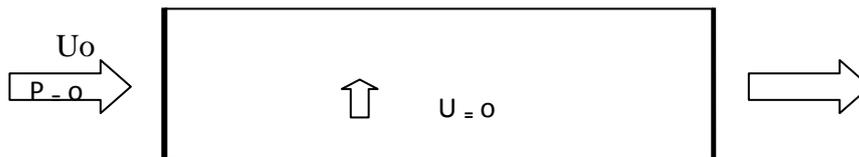


Figure 3.5: The boundary condition for the inlet fluid.

U stand for the velocity (U0) at which the fluid enters the packed bed reactor. The boundary condition (U=0 for wall) shows that there is no flow through the walls. The boundary condition P=0 for outlet shows that the pressure of the gas is determined only at the outlet points. Mass transport in the reactor is described by the diffusion-convection equations:

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (-D_i \nabla c_i + c_i u) = R_i \tag{13}$$

Where D_i denotes the diffusion coefficient (m^2/s) and c_i is the species concentration (mol/m^3). The term R_i ($mol/(m^3 \cdot s)$) corresponds to the species' net reaction rates.

In the free channel, the inlet conditions are equal to the inlet concentrations

$$c = c_{in} \tag{14}$$

At the outlet, the convective flux condition is used.

$$n \cdot (-D \nabla c) = 0 \tag{15}$$

All other boundaries, the insulating or symmetry condition are used

$$n \cdot (-D \nabla c + cu) = 0 \tag{16}$$

Balance for void fraction

The void fraction of the catalytic bed decreases as carbon is deposited. This, in turn, affects the flow through the reactor. A balance for the void fraction, or porosity, of the bed is given by (Comsol, 2008):

$$\frac{d\varepsilon}{dt} = -\frac{\varepsilon r}{M_c \rho_{soot}} \tag{17}$$

This equation can be implemented in the PDE, General Form application mode of comsol multiphysics, resulting in porosity distribution across the catalytic bed as a function of time. The initial porosity of the bed is taken to be $\varepsilon = 0.4$ (Comsol, 2008).The porosity is related to the permeability of the porous domain by the expression (Borisova and Adler, 2005):

$$k = k_o \left(\frac{\varepsilon}{\varepsilon_o}\right)^{3.55} \tag{18}$$

In this way, the porosity balance couples the mass and momentum balances describing the reacting system.

Properties of the fluid

The material properties of the fluid specified in Comsol (2008). For the reacting fluid and product is shown in Table 3.

Table 3 The transport and kinetic properties specified in Comsol for the reacting Fluid and product.

Name	Expression	Description
u_in	0.667[mm/s]	Average inlet velocity
c_CH4in	50[mol/m ³]	Inlet concentration, CH ₄
c_H2in	0[mol/m ³]	Inlet concentration, H ₂
ρ	1[kg/m ³]	Density, fluid
μ	1e-5[Pa*s]	Dynamic viscosity, fluid
ε	0.47	Porosity of zeolite Y catalyst bed
kappa	1.39e-9[m ²]	Permeability of clean zeolite Y
ρ_soot	4e3[kg/m ³]	Density of soot deposits
M_C	12.011[g/mol]	Molar weight of carbon
D_CH4	1e-6[m ² /s]	Diffusion coefficient, CH ₄
D_H2	4e-6[m ² /s]	Diffusion coefficient, H ₂
k_eff	0.1	Effectiveness factor
u_in	0.667[mm/s]	Average inlet velocity
c_CH4in	50[mol/m ³]	Inlet concentration, CH ₄
c_H2in	0[mol/m ³]	Inlet concentration, H ₂
ρ	1[kg/m ³]	Density, fluid

Meshing

In this step, the computational domain is divided into small simple shapes (known as elements) to help solve the governing equations numerically. The initialize mesh created in comsol is shown in Figure 3.4



Concentration
(mol/dm³)

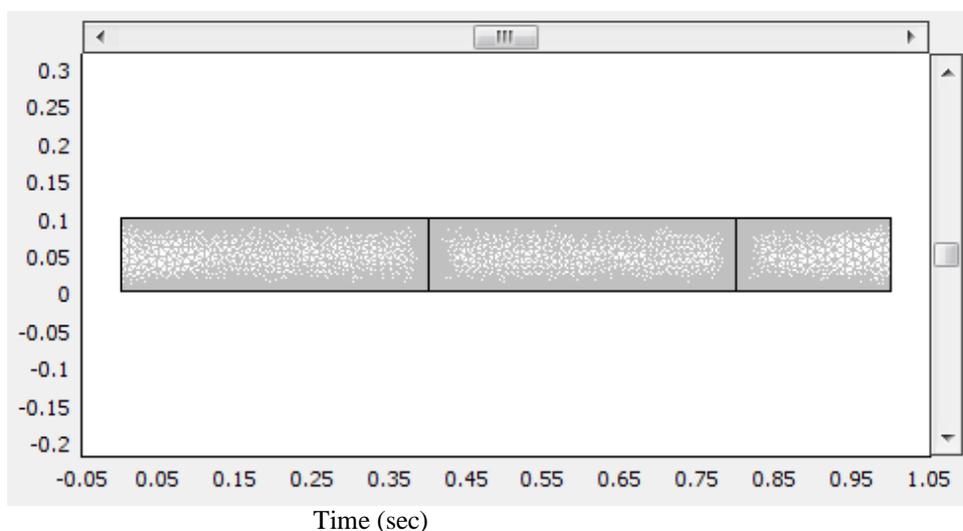


Figure 5: The Initialize mesh of the FCC packed bed reactor surface geometry.

The mesh statistics is given below:

Table 4 Mesh statistics

Mesh Statistics	Values
Number of degree of freedom	131860
Number of mesh points	7306
Number of elements	13580
Number of boundary element	1130
Number of vertex element	8
Minimum element quality	0.7994
Element area ratio	0.0090

Time step

The time problem solved is transient type and hence a time interval of 1000 sec was specified at time interval of 1 sec interval was also specified in comsol.

Solver

Comsol use the Boundary Difference Formula (BDF) to solve the set of algebraic equations obtained from the original partial differential equations in the processing stage where there are a number of different solvers available. Comsol set the minimum and maximum BDF order to 1 and 5 respectively. Elimination was selected in the constraint standing order while Automatic was selected in the Null-space function.

Tolerance

In order to control the error in the calculated solution, relative and absolute tolerance of 0.01 and 0.001 were specified in Comsol.

Processing

The governing partial differential equations are transformed into a system of algebraic equations and the unknown values (concentration) were determined.

Post processing

This step involves visualizing the solution obtained at the processing where the concentration in mol/mm^3 was specified for each parametric study of methane, hydrogen and carbon deposited. The type of plot selected in the plot parameter is the surface plot.

Numerical methods

All the governing equations were numerically solved in comsol multiphysics (version 3.5) using a stationary solver with a direct (UMFPACK) linear solver system. The residual convergence was limited to 10^{-6} for all variables. Grid independence was achieved at 57 000 finite elements (Figure 4), after which the change in the maximum temperature was less than 0.1%, change in maximum velocity was less than 1%, concentration was less than 0.1%.

III. Result And Discussion

Results

The results of the computational fluid dynamics of transport and reaction on the active surface of Zeolite Y catalyst in an FCC riser are shown below:

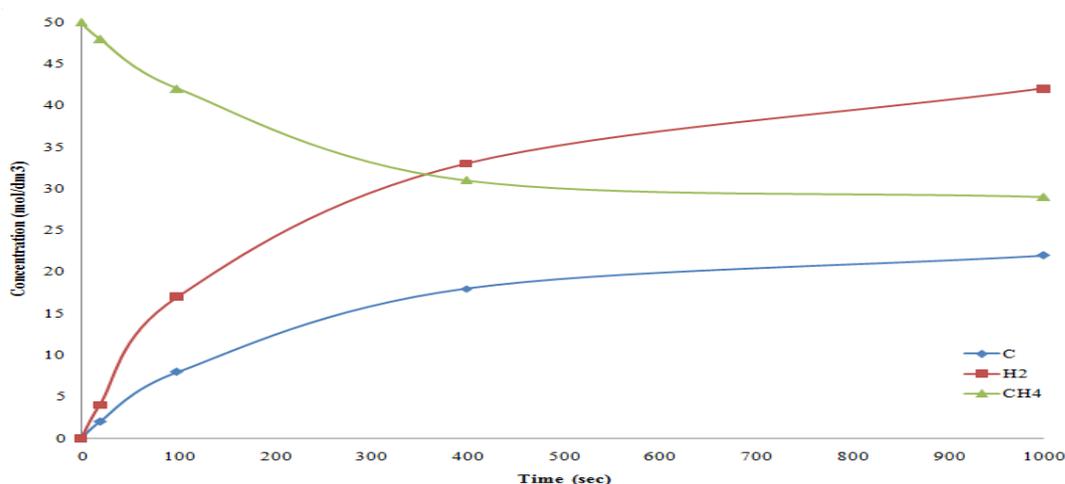


Figure 6: The concentration transients of methane decomposition over a zeolite Y catalyst.

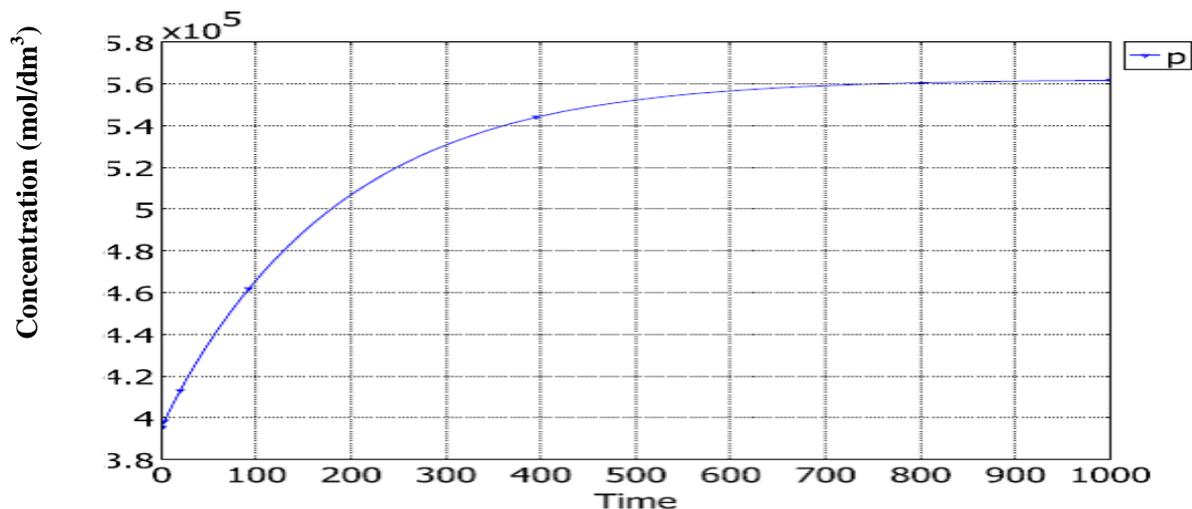


Figure 7: The variation of reactor pressure without catalyst deactivation taking place.

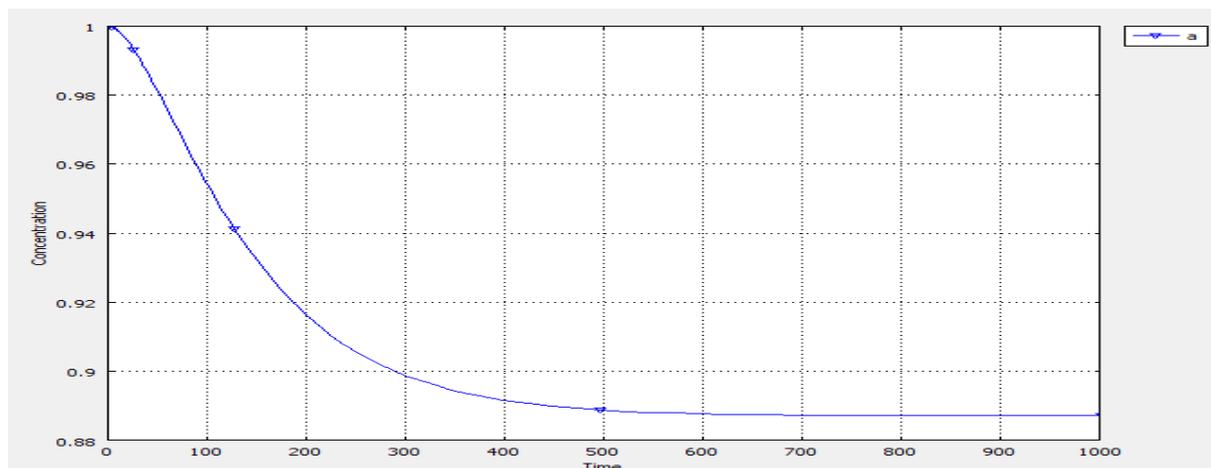


Figure 8: Catalyst activity drops off as carbon deposits at the catalyst surface.

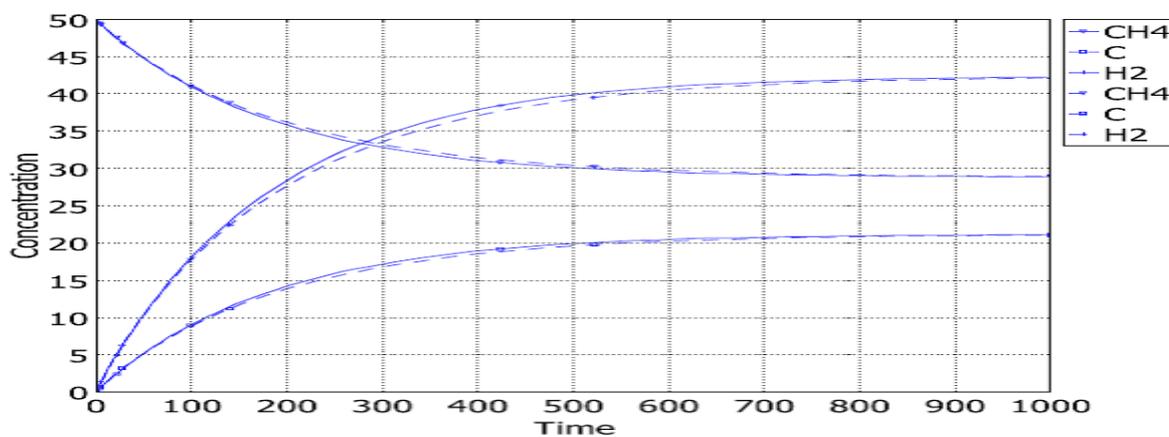


Figure 9: Concentration transients of methane, hydrogen, and deposited carbon with no deactivation present (solid lines) and with deactivation taken into account (dashed lines).

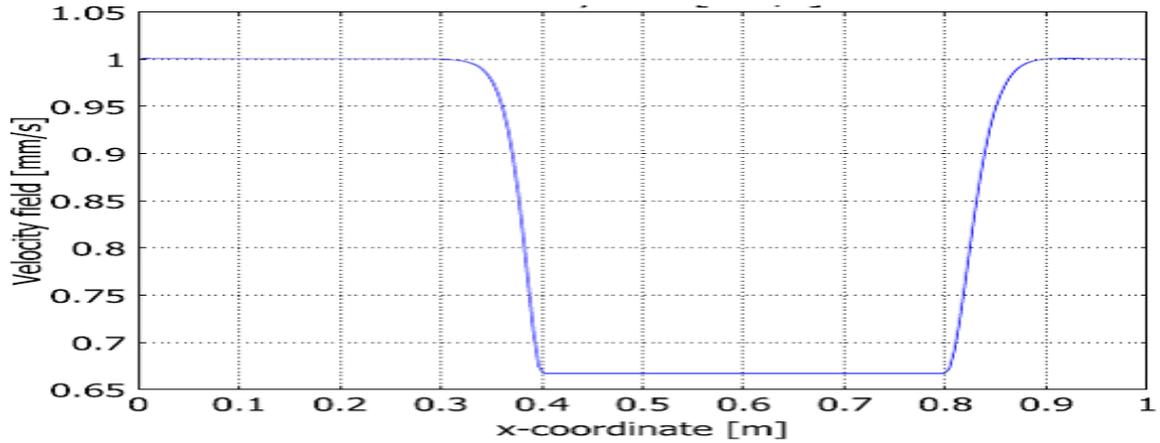


Figure 10: The variation of velocity flow field in the 2D reactor domain.

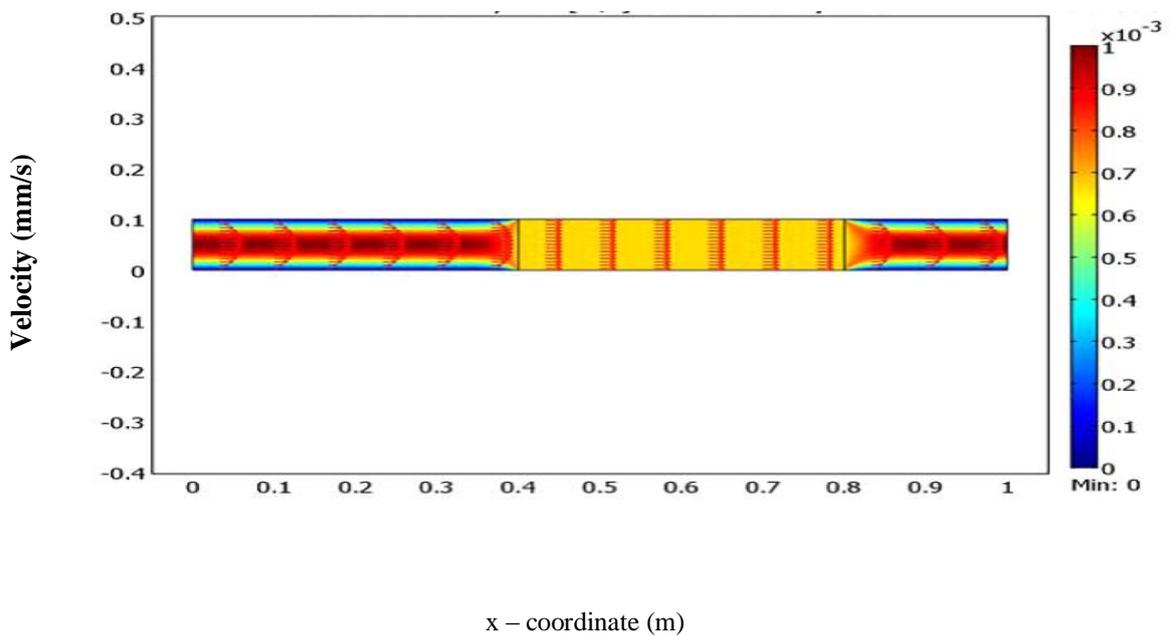


Figure 11: The variation of gas velocity along the reactor centerline.

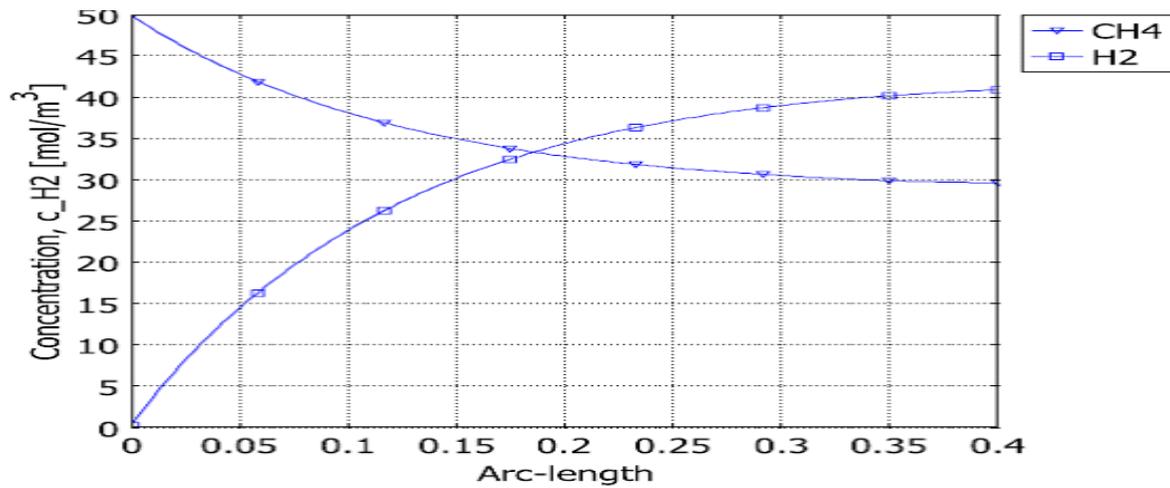


Figure 12: Methane and hydrogen concentrations as a function of the bed position.

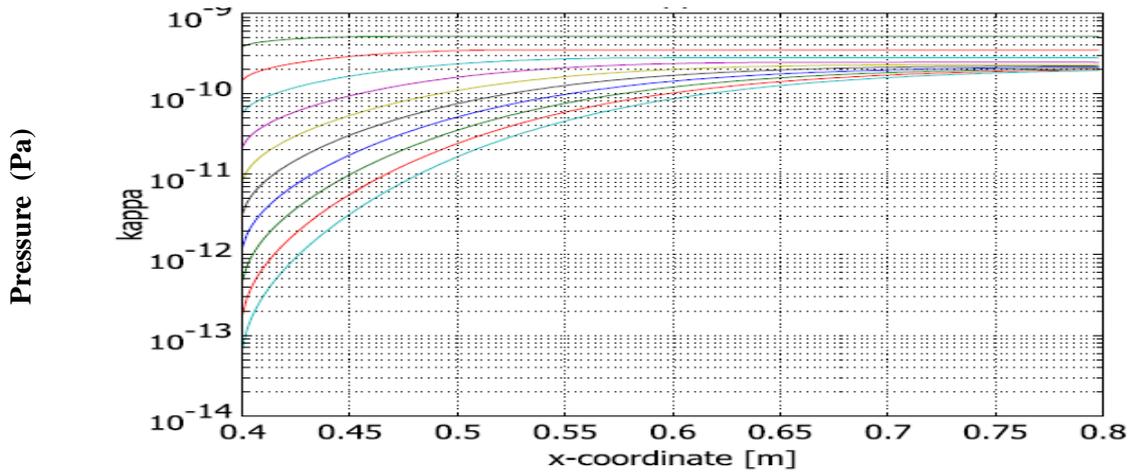


Figure 13: Permeability of packed catalytic bed as the decomposition of methane proceeds for 1,000s. Then time interval between each line is 1.

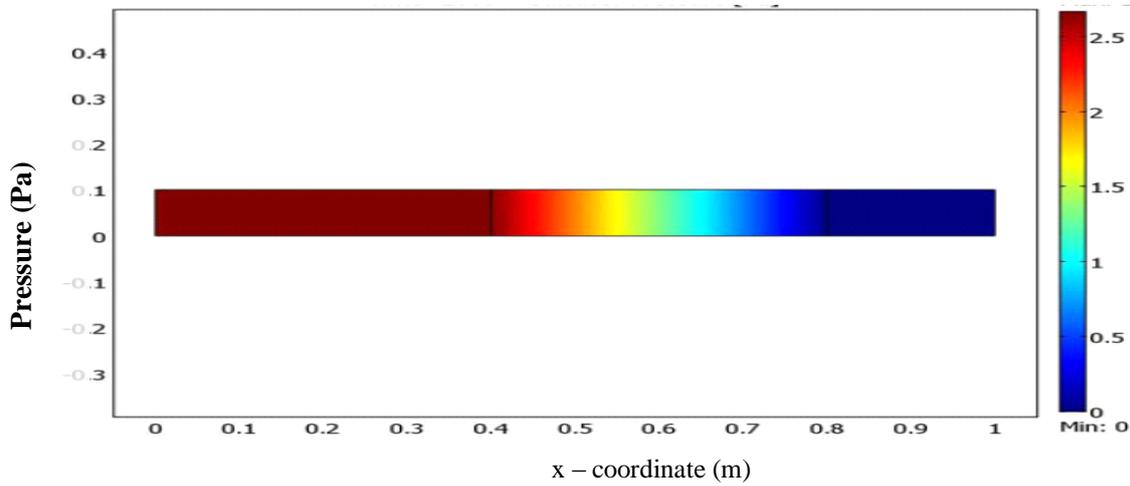


Figure 14: Distribution of pressure as a non reacting gas passes a clean catalyst be Pressure distribution across the 2D reactor domain.

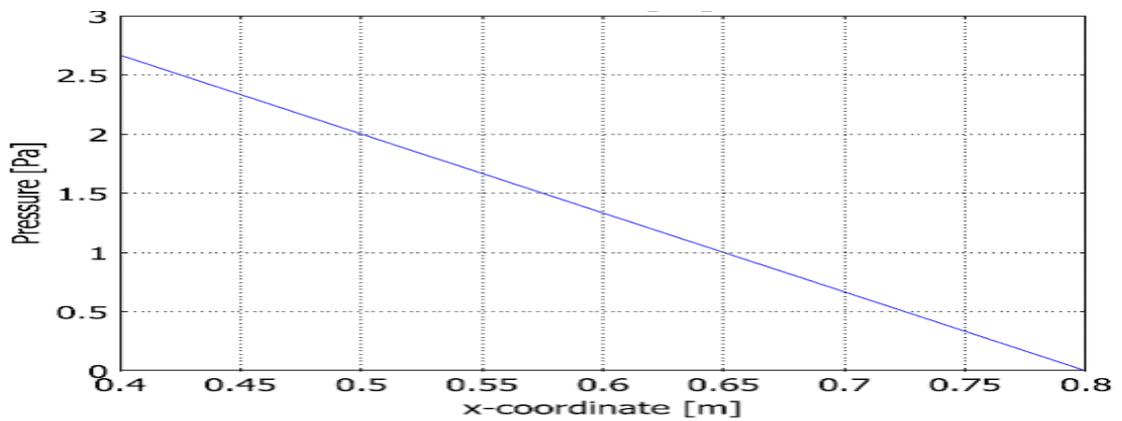


Figure 15: Pressure drop along the packed catalyst bed.

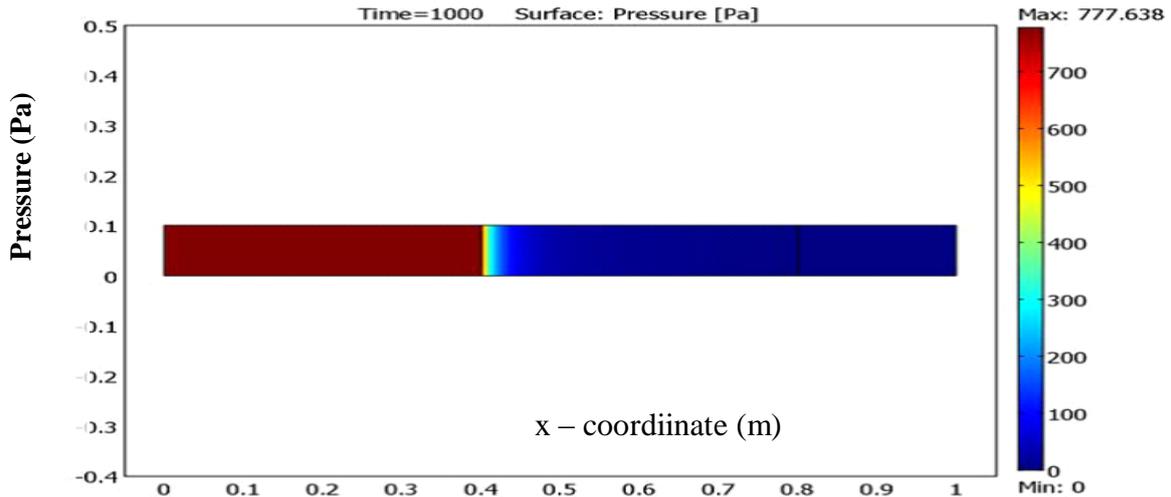


Figure 16: Distribution of pressure when methane decomposition has been allowed to occur for 1000 s (Pressure distribution across the 2D reactor domain).

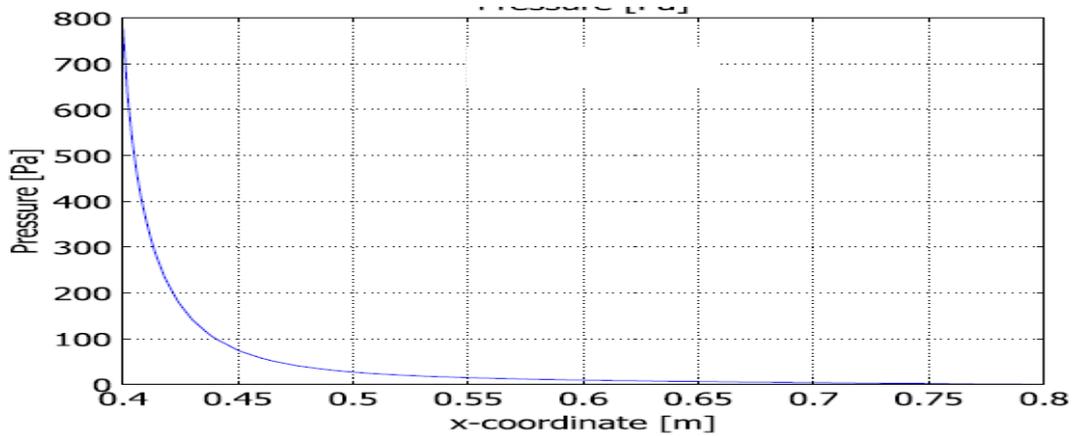


Figure 17: Distribution of pressure when methane decomposition has been allowed to occur for 1000 s (Pressure drop along the packed catalyst bed).

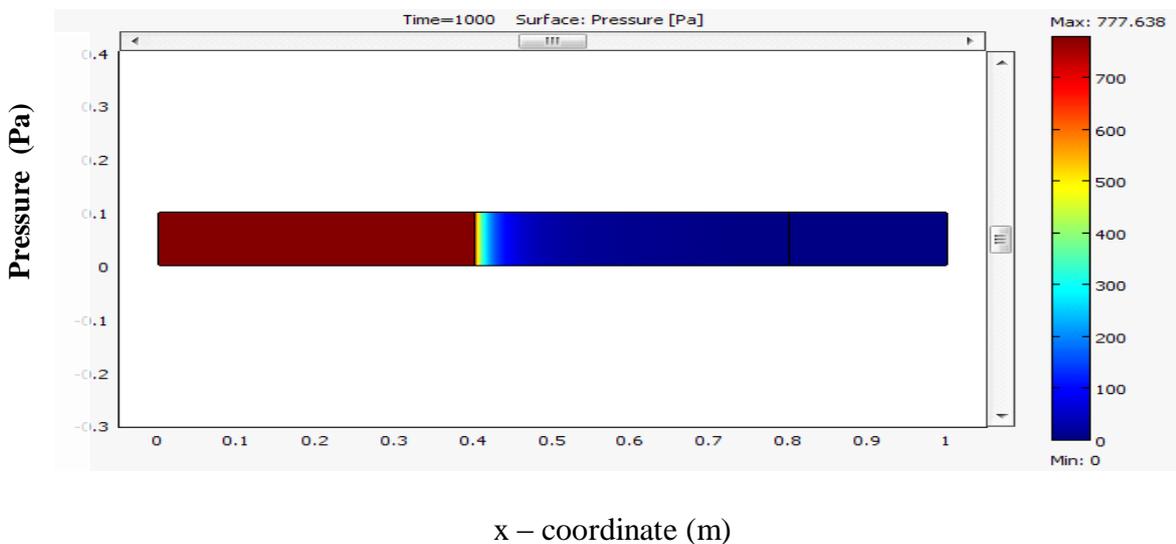


Figure 18: Distribution of pressure when methane decomposition has been allowed to occur for 1000 s (COMSOL, 2008)

Discussion of Results

Figure 6 shows the concentration profile of methane decomposition over a zeolite Y catalyst the plot shows that as the time of methane decomposition increase from 0 to 1000 s, the concentration of carbon and hydrogen formed increase from 0 to 42 mol/dm³. For hydrogen and carbon increase from 0 to 21 mol/dm³ this shows that the formation of hydrogen is faster than that of carbon. Figure 4.1 also shows that as a reaction time increase from 0 to 1000 s the methane concentration decrease from 50 to 29 mol/dm³. This shows that methane decomposition take place in the reactor. Also from Figure 6 the carbon deposition on catalyst is faster from time 0 to 400 s above 500 s carbon deposition is lower.

Figure 7 shows the pressure of the gas entering the reactor before the deposition of the catalyst. The pressure increase from 0 to 1000 s as the pressure increase from 3.6 E-5 pa to 5.6 E-5 pa. Figure 7 also shows that the pressure increase was faster from the period of 0 to 500 s but slower from time interval of 100 to 1000 s

Figure 8 shows the variation the catalyst activity with respect to time Figure 8 shows that the catalyst activity drop off as carbon deposit at the catalyst surface this shows that the catalyst deposit affect the performance of the catalyst.

Figure 9 shows the concentration transients of methane hydrogen with catalyst deactivation included in the model and when catalyst deactivation was not included in the model. The dashed line shows when catalyst deactivation was taken into an account and solid line shows when catalyst deactivation was not taken into an account. Figure 9 shows that the concentration of carbon and hydrogen formed is less when catalyst deactivation is taken into an account compare to when catalyst deactivation was taken into an account. It can be deduce from the above discussion that carbon deposit on the catalyst affect the performance of the catalyst.

The following results concern a space- and time-dependent model simulated in comsolmultiphysics. Methane decomposition occurs in a porous region where solid catalyst particles are packed. Figures 10 and 11 show the velocity field across the reactor prior to carbon deposition. The 2D plot in Figure 10 shows that the velocity profile is parabolic in the free channel sections and close to constant in the porous domain. The line plot in Figure 11 shows the velocity along the reactor centerline.

Reactions take place in the packed catalytic bed located in the reactor mid section. Figure 12 shows the concentration profiles along the centerline of the bed. The methane and hydrogen concentrations are equal approximately 0.18 m into the bed. Figures 10 and 11 show that the velocity in the bed is about 0.67 mm/s, corresponding to a residence time of 270 s. This result agrees with the findings from the reactor simulation, shown in Figures 6 and 7. Now, consider the effects as methane is constantly supplied to the reactor for 1000 seconds. The initial permeability is a constant $1.39 \cdot 10^{-9} \text{ m}^2$ across the bed. The permeability at the front end of the bed changes by four orders of magnitude during the first 1000 s of carbon deposition. As carbon deposits in the reacting bed, the pressure distribution across the reactor is affected. Figures 14 and 15 shows small, linear pressure drop as unreacting gas passes through a clean catalyst bed. Figures 16, 17 and 18 show the pressure distribution across the reactor after methane decomposition has occurred for 1000 s. The pressure drop is notably greater and occurs across the first 10 cm of the bed.

Comsol also carried out similar work on methane decomposition on Ni/Al₂O₃ catalyst which motivated this work to see the effect of carbon deposition on a different catalyst. The catalyst considered in this work is Zeolite Y catalyst. The result obtained in this work was also compared to that obtained in literature (Sharif, et al 2008) and the two results are in agreement.

IV. Conclusion

This research work demonstrate the use of computational fluid dynamic (CFD) to examine the effects of carbon deposit on fluid catalytic cracking (FCC) catalysts and the effects of the fluid flow in fluid catalytic cracking FCC reactor. Reaction was carried out in the packed catalytic bed located in the reactor's mid section with methane and hydrogen of equal concentrations of 0.18m in bed. Methane decomposition occurs in a porous region where solid catalyst particles are packed. Carbon was deposited on Zeolite Y catalyst due to decomposition of methane to carbon hydrogen in a packed bed FCC reactor. There was a moderate drop in activity of the Zeolite Y catalyst leading to a largely unaffected overall process for decomposition of methane to carbon hydrogen in a packed bed FCC reactor. The permeability at the front end of the bed changes by four orders of magnitude during the first 1000 s of carbon deposition.

Acknowledgements

From him (Allah) we come and to him we shall return (Allah). I believe in him, I worship him, I magnify his position, I glorify his name, I bear witness that there is no diety worthy of worship except him and that prophet Mohammad (PBUH) is his final messenger and I sincerely thank him for his unlimited strenght giving to me to overcome this challenge.

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