Mathematical Modeling and Simulation of the Dehydrogenation of Ethyl Benzene to Form Styrene Using Steady-State Fixed Bed Reactor

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Abstract

In this research, two models are developed to simulate the steady state fixed bed reactor used for styrene production by ethylbenzene dehydrogenation. The first is one-dimensional model, considered axial gradient only while the second is two-dimensional model considered axial and radial gradients for same variables.

The developed mathematical models consisted of nonlinear simultaneous equations in multiple dependent variables. A complete description of the reactor bed involves partial, ordinary differential and algebraic equations (PDEs, ODEs and AEs) describing the temperatures, concentrations and pressure drop across the reactor was given. The model equations are solved by finite differences method. The reactor models were coded with Mat lab 6.5 program and various numerical techniques were used to obtain the desired solution.

The simulation data for both models were validated with industrial reactor results with a very good concordance.

Keywords: Fixed bed reactor, two dimensional models, Simulation, Steady-state, Methylbenzene dehydrogenation.

التمثيل الرياضي والمحاكاة لتفاعل سحب الهيدروجين من الأثيلِ بنزينِ لتكوين الستايرينِ باستعمال مفاعلَ الطبقة الثابتِة المستقر

الخلاصة

في هذا البحث تم تطوير نموذجين لمحاكاة مفاعل الطبقة الثابتة في الحالة المستقرة لانتاج الستارين بتفاعل سحب الهيدروجين من الاثيل بنزين. النموذجُ الأول أحادي البعد وياخذ بنظرالاعتبارطول المفاعل فقطُ بينما النموذجُ الثاني ثنائي الأبعادُ وياخذ بنظر الاعتبار الطول ونصف القطر للمفاعل.

النماذج الرياضية المطورة شَملتْ المعادلاتِ الآنيةِ اللاخطّيةِ في المتغير المتعدّدِ المعتمد. تم توصيف المفاعل بشكل كامل وذلك بحل مجموعة من المعادلات الجزئية والتفاضلية والجبرية لايجاد توزيع التراكيز ودرجة الحرارة والضغط داخل المفاعل. تمت برمجة النماذج الرياضية باستخدام برنامج ماثلاب الاصدار(6.5) وباستخدام تقنيات عددية مُخْتَلِفة لايجاد الحَلِّ المطلوبِ.

بعد مقارنة النتائج النظرية المستحصلة من النماذج النظرية مع النتائج العملية الماخوذة بنفس الظروف التشغيلية اتضح ان هناك تطابق كبير بين النتائج النظرية و النتائج العملية.

الكلمات الدالة: مفاعل الطبقةِ الثابتِة، نموذج ثنائي الأبعاد، محاكاة،الحالة المستقرة، سحب الهيدروجين من الاثيل بنزين.

Nomenclature

A Rate constant, $m^6/(mol \cdot kg \cdot s)$
$a_1,a_2,.a_5$ Constants of material balance equation, -
$b_1,b_2,.b_5$ Constants of energy balance equation,-
C_i Concentration of component I, mol/m^3
Cp Specific heat of the gas, J/kg.K

$D_{A,m}$ Diffusivity of component A in mixture (m^2/s)
Dp Diameter of the catalyst pellet, m
D_m Molecular diffusion coefficient, m^2/s
E Activation energy, J/mol
F_i Molar feed flow rate for component I, mol/s
G Superficial velocity, $kg/m^2.s$
ΔH_{Rx} Heat of reaction, J/mol
K Reaction rate constant, $kmol/s.kg\ cat.bar^n$
K_e Thermal conductivity, w/m.k
K_{eq} Equilibrium constant, bar
L Reactor length, m
M_{wi} Molecular weight of component I, g/mol
P Pressure, N/m^2 or bar
R Radial coordinate, m
r_i Reaction rate, $kmol/m^3.s$
R Gas constant, 8.3144 J/ mol.K
Rp Particle radius, m
Sg Total surface area, m^2/kg
t Time, s
T Temperature, K
T_R Reference temperature, K
U Velocity, m/s
V Reactor volume, m^3
V_i Molar volume of component I, m^3/mol
y_i Gas phase mole fraction of component i (-)
z Reactor axial coordinate, m

Greek letters

ϕ_{ij} Wilke interaction coefficients, (-)
ρ Gas density, kg/m^3
μ Gas viscosity, g/m.s
ν_{ij} Stoichiometric coefficient of the i th component in the j th reaction, (-)
Δ Difference, (-)
ε_b Bed voidage fraction, (-)
ε_s Pellet porosity, (-)
ρ_{Cat} Catalyst density, kg/m^3
ρ_p Pellet density, kg/m^3
σ Pellet constriction factor, (-)
σ_c Constriction factor, (-)
τ Tortuosity factor, (-)

Subscripts , Superscripts

0 Inlet , Initial
B Bed
cat Catalyst
e Effective
g Gas phase
H_2 Hydrogen
I Number of components in the system
J Number of reactions considered
m Radial direction index
n Axial direction index
p Catalyst Particle

Abbrevations

AE Algebaric Equation
DE Differential Equation
EB Ethylbenzene
ODE Ordinary differential Equation
PDE Partial Differential Equation
ST Styrene

Introduction

Styrene is one of the most important monomers used as a raw material for synthetic polymers. The recent worldwide production of styrene is estimated at more than 15 million tons per year [1, 2]. Ninety percent of the world production of styrene is manufactured by the catalytic dehydrogenation of ethylbenzene over iron oxide catalysts. The main reaction is endothermic and reversible and severely limited by the thermodynamic equilibrium. The maximum ethylbenzene conversion reported is less than 50% [2].

Simulation is the technical discipline which shows the behavior and reactions of any system on its model.

Computer simulation starts with creation of a mathematical model and the obtained equations are solved by using an appropriate method. Most of the chemical processes have nonlinear properties [3].

The model of any system is usually represented by the set of the differential equations. Steady-state means that derivatives with respect to time are equal to zero. On the contrary, dynamic state is the response to the change of the

input variable. The fixed bed reactors are typically described by nonlinear partial differential equations (PDE's). The main source of nonlinearities is concentrated in the kinetics terms of the model equations. Other reason for this nonlinearity is the sensitive and intricate characteristics of the reactor system caused by the heat of reaction nonlinearly dependent on the bed-temperature [4].

Sheel and Crowe (1969) [5] are the first who reported on modeling and optimization of an industrial styrene reactor. They employed six reactions with a pseudo homogeneous model for modeling both adiabatic and steam-injected reactors. Sheel and Crowe used Rosenbrock's multivariable search technique to optimize a profit function with steam temperature, steam rate, and bed length as the decision variables.

Clough and Ramirez (1976)[6] developed a mathematical model for a styrene pilot plant reactor based on the main reactions selected by Sheel and Crowe (1969) [5]. They used a steady state model to optimize the location of a steam injection port for adiabatic and steam-injected reactors.

Sheppard et al. (1986)[7] developed a model to simulate an industrial ethylbenzene dehydrogenation reactor using several kinetic models. The optimum operating conditions are explored for one and two-bed reactor configurations by using two industrial catalyst systems. This model was then used to locate the optimum inlet temperature and steam to oil ratio for a specified styrene selling price and a set of material and operating costs. They used the model to investigate the economics of installing a two-bed reactor system and they conclude that the economics of using a high selectivity catalyst are superior to the high activity catalyst.

Elnashaie et al. (1993)[8] developed a rigorous heterogeneous model for the reactor based on dusty gas model (Stefan-Maxwell equations) for diffusion and reaction in the catalyst pellets. This model was used to extract intrinsic kinetic constants from industrial reactor data iteratively. Elnashaie and Elshishini (1994)[9] employed both pseudo-homogeneous and hetero-geneous models for simulating an industrial styrene reactor. Both works used the six reactions employed by Sheel and Crowe (1969) [5].

Lim et al. (2002)[10] modeled successfully styrene monomer production process in an adiabatic redial flow reactor. To overcome the difficulties of the lack of internal or intermediate measurements of the industrial reactor and also the lack of experimental results of the catalyst deactivation, they proposed a hybrid model in which the mathematical model is combined with neural networks. Using this model, they easily determined optimal operating conditions and testing new operating conditions. On the situation of changing catalyst, this simulator shows good performance because the catalyst parameters are updated using current process data.

Yee et al. (2002)[11] modeled the industrial reactor in Elnashaie and Elshishini (1994)[9] by both pseudo-homogeneous and heterogeneous models. They successfully used the rate expressions and kinetic data for six reactions as well as other required data given by Elnashaie and Elshishini (1994) [9]. The results obtained by Yee et al. (2002) [11] showed that both the models predicted reactor exit conditions comparable to the industrial data as well as to those reported in Elnashaieand Elshishini (1994) [9].

Li et al. (2003)[12] formulated multiobjective optimization of styrene reactors design for both adiabatic and steam-injected. Their results of multiobjetive optimization showed that objectives, production rate and selectivity can be improved compared to the current operating conditions. As expected, steam injected is found to be better than adiabatic operation.

Tarafder et al. (2005)[13] performed modeling, simulation and optimization of an industrial styrene reactor plant by using the corrected kinetic model of Sheel and Crowe (1969)[5], Elnashaie and Elshishini (1994)[9]. The model details are the same as in Elnashaie and Elshishini (1994)[9] and Yee et al. (2002) [11]. The simulation results are very close to industrial styrene reactor results and the minor differences are due to differences in physical properties.

Lee (2005)[14] in his thesis makes a detail study for reaction kinetic, design and simulation of industrial ethyl-benzene dehydrogenation reactor. Kinetic experiments are carried out using a commercial potassium-promoted iron catalyst in a tubular reactor under atmospheric pressure. His experimental work icluded different operating conditions, i.e., temperature, feed molar ratio of steam to ethylbenzene, styrene to ethylbenzene, and hydrogen to ethylbenzene and space time. The kinetic model yielded an excellent fit of the experimental data. He used intrinsic kinetic parameters with the heterogeneous fixed bed reactor model which is explicitly accounting for the diffusional limitations inside the porous catalyst. Finaly, he simulated multi-bed industrial adiabatic reactors with axial and radial flow and investigated the effect of the operating conditions on the reactor performance.

Ashish and Babu (2006)[15] applied multi-objective optimization study for industrial styrene reactor using Multi-Objective Differential Evolution (MODE) algorithm. Two objective optimization studies is carried out using objective functions, namely production, yield and selectivity of styrene for adiabatic as well as steam-injected reactors. Their model is defined by six equations from material balance, one equation of energy balance, and one of pressure drop. All kinetic data and model equation are taken from Elnashaie and Elshishini (1994)[9], Yee et al. (2002) [11], and Babu et al. (2005)[16]. The results showed that the objective functions such as styrene flow rate, yield, and selectivity can be improved by adapting optimal operating conditions.

The purpose of this work is the development of a model to simulate an industrial ethylbenzene dehydrogenation reactor. This study takes into consideration modeling fixed bed reactor using two models (one dimension and two dimensions) and then comparing the results of these two models with experimental results.

Case study

Styrene can be produced by catalytic dehydrogenation of ethyl-benzene, in this operation ethylbenzene is mixed with saturated steam and preheated by heat exchange with the reactor effluent. Major portion of saturated steam is superheated to about 1000 K in a furnace. The hot ethyl-benzene plus steam stream and this superheated steam to reactor inlet temperature of over 875K are injected into the fixed bed catalytic reactor [12].

Superheated steam is present in excess, usually added at a molar ratio of 15:1. The overall effects of the increase of the steam/hydrocarbon ratio are to increase the selectivity for styrene at the same level of conversion and the lifetime and stability of the catalyst. The advantages of using steam are [14]:

1. Steam can provide the heat to maintain the reaction temperature.
2. Steam acts as a diluent to shift the equilibrium conversion to higher value through a decrease of the partial pressures of ethylbenzene and hydrogen.
3. Steam removes the carbonaceous deposition by the gasification reaction.

The reactor effluent is cooled to stop the reactions and then sent to the separation section to recover styrene and unconverted ethylbenzene for recycle [12].

Fixed Bed Reactor Models

One-dimensional Model

In one-dimensional model, radial variations of concentration and temperature are not considered. Industrial reactors have high axial aspect (Length/Diameter) ratio. The radial dispersion of concentration and temperature within the reactor bed is negligible. Thermophysical properties like the density and velocity of the gas phase vary due to temperature, pressure and mole changes. The reaction rate constants vary with temperature exponentially. Axial variations of the fluid velocity arising from the axial temperature changes and the change in number of moles due to the reaction are accounted by using the continuity and the momentum balance equations [17].

Most of previous papers assume that there are no radial variations in velocity, concentration, temperature and reaction rate in the fixed bed reactors [5, 6, 12].

Froment et al. (1990)[18] suggested a void fraction profile induces a radial variation in fluid velocity. Hoiberg et al. (1971)[19] confirmed that packed beds with radial aspect ratio lesser than 50 showed negligible radial variations of velocity.

To obtain the solution for the fixed bed reactor the set of ordinary differential equations (ODEs) which represent heat, mass and momentum balances are solved simultaneously. The reactor is divided into several subvolumes. Within each subvolume, the reaction rate is considered to be spatially uniform. The molar flowrates are found by solving the set of component material balances equations.

$$\frac{dF_i}{dV} = -\sum_{j=1}^{Nreacction} v_{ij} r_j \qquad \ldots\ldots\ldots\ldots (1)$$

The heat balance for fixed bed reactor gives the follwing equation [18]:

$$\frac{dT}{dV} = \frac{\sum_{j=1}^{Nreaction} (-r_j) * [-\Delta HR_j(T)]}{\sum_{i=1}^{Nc} F_i Cp_i} \qquad \ldots\ldots\ldots\ldots (2)$$

The pressure drop in fixed bed reactor calculated by using Ergun equationas below [20]:

$$\frac{dP}{dZ} = -\frac{G}{\rho D_p}\left(\frac{1-\varepsilon_b}{\varepsilon_b^3}\right)\left[\frac{150(1-\varepsilon_b)\mu}{D_p} + 1.75G\right] \ldots (3)$$

To simulate stady state fixed bed adiabatic reactor with one dimension model, the mass, heat and momentum balance equations were solved. The numerical Runge-Kutta integration method was used to solve the ordinary differential equations to describe molar flow rates, temperature and pressure profile along the length of the reactor. Equations (1 - 3) are solved simultaneously with reaction kinetic equations for each component. The reactor is divided into 161 sub-volumes to reach a required accuracy. Decreasing the number of sub-volumes will reduce the solution accuracy, while increasing the number of sub-volumes does not have any significant effect on accuracy.

The flow chart of simulation program for both two models is shown in Fig. (2). A subroutine Matlab ODE45 is used to integrate all the model equations along the length of reactor.

Two-dimensional Model

Fixed bed reactors are economically attractive because its geometrical simplicity leads to low operational and fixed costs. The large heat transfer surface area of the tube is particularly advantageous for strongly exothermic reactions. Despite of these advantages, the disadvantages of plug flow reactors are that temperatures are hard to control due to the large radial temperature gradients developed along the reactor when high conversion values are obtained [17].

The two-dimensional (axial and radial gradients) model developed for the fixed bed reactor. This model considers heat and mass transfer in the radial and axial directions. The density and diffusity of reaction mixture were considered as a function of some local properties.

The two-dimensional model result a system of non linear ordinary differential equations which solved by numerical methods through a routine that uses the finite differences method.

Assumptions

In two-dimensional model the concentration of any species and the temperature inside the fixed bed reactor can vary with axial position (z) and radial position (r). The physical properties of the fluid (density, viscosity, thermal conductivity, heat capacity, reaction enthalpy), and the coefficients of heat and mass transfer vary along the reactor length. The major assumptions of two-dimension model are as follows:

1. The system is steady state therefore the variation with time is negligible.
2. The variation in the angular direction is negligible. Therefore, the concentrations and temperatures are only functions of axial and radial position.
3. Gas properties are functions of temperature and pressure.
4. The physical properties of the solid catalyst are taken as constant.
5. The packed bed is assumed to be uniformly packed with negligible wall effects.
6. No reaction except catalyst bed.
7. Plug-flow velocity profile.
8. Ideal gas.

Kinetics of Ethylbenzene Dehydrogenation

In the styrene production reactor, six reactions are carried. The main reacion is reversible while the others is irreversible reacions.

$$C_6H_5CH_2CH_3 \xleftrightarrow{k_1} C_6H_5CHCH_2 + H_2 \quad \ldots (4)$$

$$C_6H_5CH_2CH_3 \xrightarrow{k_2} C_6H_6 + C_2H_4 \quad \ldots\ldots (5)$$

$$C_6H_5CH_2CH_3 + H_2 \xrightarrow{k_3} C_6H_5CH_3 + CH_4 \quad . (6)$$

$$0.5C_2H_4 + H_2O \xrightarrow{k_4} CO + 2H_2 \quad \ldots\ldots (7)$$

$$CH_4 + H_2O \xrightarrow{k_5} CO + 3H_2 \quad \ldots\ldots\ldots (8)$$

$$CO + H_2O \xrightarrow{k_6} CO_2 + H_2 \quad \ldots\ldots\ldots (9)$$

The reactions rate constants, which have been employed in the present study, are summarized in Table (1). These constants have been determined by applying a reactor model which its predictions were compared with 50 working days data of a styrene plant by Sadeghzadeh et al. (2004) [21].

Generally, Fe_2O_3 catalyst promoted with K_2CO_3 and Cr_2O_3 or CeO_2 was used for dehydrogenation of ethylbenzene and different compositions of this catalyst results in different kinetic parameters. Since the dehydrogenation of ethyl-benzene is a reversible endothermic reaction, high styrene yield is favored by high temperature [11].

Model Equations

Component Mole Balance

The cylindrical shell of thickness Δr and length Δz in fixed bed reactor is represented in Figure (1). The reactants fed in specific molar flow rates from one

side and exit after reaction with products from the other side. Based on the general mass and energy balance equations reported by Bird et al. (2002)[22], the generalised expression for the dynamic mole balance for the individual components within the elemental volume of length dz is given by equation (10). The transfer of moles occurs due to bulk flow and diffusion. The number of moles of each component at any instant in the elemental volume is the product of the individual molar concentration and the elemental volume at that instant. The fluid velocity varies with position. The diffusive mass transfer rate is given by the Fick's first law.

$$D_e\frac{\partial^2 c_i}{\partial r^2}+\frac{D_e}{r}\frac{\partial c_i}{\partial r}+D_e\frac{\partial^2 c_i}{\partial z^2}-U_z\frac{\partial c_i}{\partial z}+r_i=\frac{\partial c_i}{\partial t} \quad (10)$$

The velocity profile is given by the following equations:

For plug flow

$$U_Z=U_0 \quad \ldots\ldots\ldots (11)$$

For laminar flow

$$U_Z=2U_0\left[1-\left(\frac{r}{r_o}\right)^2\right] \quad \ldots\ldots\ldots (12)$$

At steady state $\frac{\partial c_i}{\partial t}=0$

then Equation (10) will be:

$$D_e\frac{\partial^2 c_i}{\partial r^2}+\frac{D_e}{r}\frac{\partial c_i}{\partial r}+D_e\frac{\partial^2 c_i}{\partial z^2}-U_z\frac{\partial c_i}{\partial z}+r_i=0 \quad \ldots (13)$$

The first and second order partial differentials appearing in equation (13) are defined in terms of discretized variables as follows:

$$\left(\frac{\partial c_i}{\partial r}\right)_{m,n}=\frac{C_{i(m+1,n)}-C_{i(m-1,n)}}{2\Delta r} \quad \ldots\ldots (14)$$

$$\left(\frac{\partial^2 c_i}{\partial r^2}\right)_{m,n}=\frac{C_{i(m+1,n)}-2C_{i(m,n)}+C_{i(m-1,n)}}{\Delta r^2} \quad \ldots\ldots\ldots (15)$$

Also:

$$\left(\frac{\partial c_i}{\partial z}\right)_{m,n}=\frac{C_{i(m,n+1)}-C_{i(m,n-1)}}{2\Delta z} \quad \ldots (16)$$

$$\left(\frac{\partial^2 c_i}{\partial z^2}\right)_{m,n}=\frac{C_{i(m,n+1)}-2C_{i(m,n)}+C_{i(m,n-1)}}{\Delta z^2} \quad \ldots\ldots\ldots (17)$$

Where $C_i(m,n)=C_i(r_{m,n},z_{m,n})$

By substitution equations (14 to 17) in equation (13):

$$\frac{D_e}{r}\frac{1}{2\Delta r}\left(C_{i(m+1,n)}-C_{i(m-1,n)}\right)+\frac{D_e}{\Delta r^2}\left(C_{i(m+1,n)}-2C_{i(m,n)}+C_{i(m-1,n)}\right)$$
$$+\left(C_{i(m,n+1)}-2C_{i(m,n)}+C_{i(m,n-1)}\right)-\frac{U_z}{2\Delta z}\left(C_{i(m,n+1)}-C_{i(m,n-1)}\right)+r_i=0$$

$\ldots\ldots\ldots (18)$

Equation (18) re-written as:

$$C_{i(m+1,n)}(a_1+a_2)-2C_{i(m,n)}(a_2+a_3)+C_{i(m-1,n)}(a_2-a_1)$$
$$+C_{i(m,n+1)}(a_3+a_4)+C_{i(m,n-1)}(a_3-a_4)=a_5$$

$\ldots\ldots (19)$

Where

$$a_1=\frac{D_e}{r}\frac{1}{2\Delta r}$$
$$a_2=\frac{D_e}{\Delta r^2}$$
$$a_3=\frac{D_e}{\Delta z^2}$$
$$a_4=\frac{-U_z}{2\Delta z}$$
$$a_5=-r_i$$

Energy Balance

The generalised expression for the unsteady-state energy balance is given in equation (20)[22]. In the gas phase, transfer of heat occurs due to bulk flow and heat transfer by conduction. The heat content in the elemental volume is the sensible heat exchange arising due to a temperature difference. The bulk flow term arise from the temperature change due to the bulk motion of the fluid.

$$\frac{k_e}{r}\frac{\partial T}{\partial r}+k_e\frac{\partial^2 T}{\partial r^2}+K_e\frac{\partial^2 T}{\partial z^2}-\left(U\sum C_i Cp_i\right)\frac{\partial T}{\partial z}$$
$$-\Delta H_{RX}(-r_A)=\sum C_i Cp_i\frac{\partial T}{\partial t} \quad \ldots\ldots\ldots (20)$$

At steady state heat balance therefore $\partial T/t=0$ then the equation (20) will be:

$$\frac{k_e}{r}\frac{\partial T}{\partial r}+k_e\frac{\partial^2 T}{\partial r^2}+K_e\frac{\partial^2 T}{\partial z^2}-\left(U\sum C_i Cp_i\right)\frac{\partial T}{\partial z}-\Delta H_{RX}(-r_A)=0$$

$\ldots\ldots\ldots (21)$

By applying finite differences approximation, equation (21) re-written as:

$$\frac{k_e}{2\Delta r}\left(T_{(m+1,n)}-T_{(m-1,n)}\right)+\frac{K_e}{\Delta r^2}\left(T_{(m+1,n)}-2T_{(m,n)}+T_{(m-1,n)}\right)+\frac{K_e}{\Delta z^2}$$
$$\left(T_{(m,n+1)}-2T_{(m,n)}+T_{(m,n-1)}\right)-\frac{\left(U\sum Cp_i C_i\right)}{2\Delta z}\left(T_{(m,n+1)}-T_{(m,n-1)}\right)-\Delta H_{RX}(-r_A)=0$$

. . . . . (22)

Equation (22) re-written as:

$$T_{(m+1,n)}(b_1+b_2)-2T_{(m,n)}(b_2+b_3)+T_{(m-1,n)}(b_2-b_1)+ T_{(m,n+1)}(b_3+b_4)+T_{(m,n-1)}(b_3-b_4)=b_5 \quad \text{. .. . . . (23)}$$

Where

$$b_1=\frac{k_e}{2\Delta r}$$
$$b_2=\frac{K_e}{\Delta r^2}$$
$$b_3=\frac{K_e}{\Delta z^2}$$
$$b_4=\frac{U\sum Cp_iC_i}{2\Delta z}$$
$$b_5=\Delta H_{RX}r_A$$

Boundary conditions

a- At the entrance to the reactor z=0 for all r:

$T=T_o$ and $C_i = C_{io}$

b- At r=0, we have symmetry

$$\frac{\partial C_i}{\partial r}=0 \quad \text{and} \quad \frac{\partial T}{\partial r}=0$$

c- At the exit of the reactor z = L

$$\frac{\partial T}{\partial z}=0 \quad \text{and} \quad \frac{\partial C_i}{\partial z}=0$$

Physical and Thermal Properties

Diffusivity

Effective diffusivity for unimodal and narrow pore size distribution in the catalyst can be defined as in the equation **[23, 24]**.

$$D_{eff}=D_m\frac{\varepsilon_p}{\tau_p} \quad \text{. . . . . (24)}$$

Where τ is the tortuosity of the particle and it is usually in the range 2 - 4.

The diffusivity, D, is a composite of molecular diffusivity and Knudsen diffusivity, as in the equation **[14]**.

$$\frac{1}{D}=\frac{1}{D_m}+\frac{1}{D_k} \quad \text{. . . . . (25)}$$

Knudsen diffusivity in gases in a straight cylindrical pore can be calculated from the kinetic theory **[14, 18]**:

$$D_k=\frac{8}{3}\frac{\varepsilon_s}{S_g\rho_p}\sqrt{\frac{2RT}{\pi M_A}}=\frac{19400}{S_g\rho_p}\sqrt{\frac{T}{M_A}} \quad \text{. . . . . (26)}$$

The diffusion coefficients for binary gas mixtures can be calculated from the following theoretical equation based upon the kinetic theory of gases and the Lennard-Jones potential **[14]**:

$$D_{A,B}=\frac{0.001T^{1.75}(1/M_A+1/M_B)^{1/2}}{P\left[\left(\sum V\right)_A^{1/3}+\left(\sum V\right)_B^{1/3}\right]^2} \quad \text{. . . . . (27)}$$

The diffusivity of species 1 through stagnant gas mixtures 2, 3, . . ., n can be calculated by the reduced Wilke equation **[14, 25]**.

$$\frac{1}{D_{1m}}=\frac{1}{1-y_1}\sum_{k=2,3}^{n}\frac{y_k}{D_{1k}} \quad \text{. . . . . (28)}$$

Viscosity

The gas viscosity was determined using first order Chapman-Enskog kinetic theory with Wilke's approximation to determine the interaction coefficient (ϕ_{ij}) **[14, 18, 26]**.

$$\mu_m=\sum_{i=1}^{Nc}\frac{y_i\mu_i}{\sum_{j=1}^{Nc}y_i\phi_{ij}} \quad \text{. . . . . (29)}$$

Where μ_m is the viscosity of mixture, μ_i is the viscosity of pure component i, and y_i is the mole fraction of pure component i. Wilke's approximation yields **[14]**.

$$\phi_{ij}=\frac{\left[1+\left(\frac{\mu_i}{\mu_j}\right)^{1/3}\left(\frac{Mw_j}{Mw_i}\right)^{1/4}\right]^2}{\left[8\left(1+\frac{Mw_i}{Mw_j}\right)\right]^{1/2}} \quad \text{. . . . . (30)}$$

In order to evaluate gas viscosity the correlation below has been used **[26]**:

$$\mu=A+BT+CT^2 \quad \text{. . . . (31)}$$

The coefficients of viscosity polynomial for all components in this paper are given by Ludwig (2001) **[27]** as in Table (2).

Heat Capacity

In order to evaluate the vapor phase heat capacity the following correlation has been used [26]:

$$Cp_i = A_i + B_i T + C_i T^2 + D_i T^3 \quad \ldots\ldots\ldots (32)$$

The coefficients of heat capacity polynomial are found from Reid et al. (1987) [26] and given in table (3). The heat capacity of the gas mixture is calculated by equation (33):

$$Cp_m = \sum_{i=1}^{nc} Cp_i y_i \quad \ldots\ldots\ldots (33)$$

The heat of reaction is calaculated by the equation (34):

$$\Delta H_{Rx}(T) = \Delta H^{o}_{Rx}(T_R) + \int_{T_R}^{T_m} \Delta C_{Pl_i} dT \quad \ldots\ldots\ldots (34)$$

Thermal Conductivity

In order to evaluate the thermal conductivity the following correlation has been used [27]:

$$k = A + BT + CT^2 \quad \ldots\ldots\ldots (35)$$

The coefficients of this polynomial are given in table (4).

Also the viscosity of gas mixture, the thermal conductivity of the gas mixture can be as approximated by Wilke's approximation.

Numerical Solution

The system is described by three partial differential equations (mass balance, energy balance and momomentum balance) on two dimensional surfaces. This surface represents a cross-mintion of the fixed bed reactor in the z-r-plane.

The borders of the two- dimensional surface represent the inlet, outlet, the wall of the reactor and the center line. This means that the three differential equations only will be solved for half of the reactor because of axisymmetrical of the reactor. Finite differences approximation with Gaussian elemenation method was used to solve this set of PDEs.

To predict the concentrations of single components within the reactor, all reactions must be taken into consideration. Equation (19) are written for all of points within the reactor taken into consideration the initial and boundary condititons for mass transfer, then these equations are solved by using Gaussian elemenation method. These steps are repeated for all other reactants and products within the reactor.

Similarity the heat balance equation (23) are written for all points in the reactor taken into considration the initial and boundary conditions for heat balance, then these equations are solved simultaneously to predict temperature distribution within the reactor.

The pressure distribution is found by solving equation (3) for one dimension.

The three above steps are repeated several times until the desired accuracy is reached. The accuracy depends on the calculated temperature and the program is stoped when the statement in equation (36) applied:

$$\sum (T_i^j - T_i^{j-1}) \le 0.01 \sum T_i^j \quad \ldots\ldots\ldots (36)$$

The number of total points is a result of multipling the number of points radialy by number of points axially. The total number of points was adjusted to obtain the desired accuracy, for high resolution 20 points in the radial direction and 50 points in the axial direction is used.

The flow chart of simulation program for both two models is shown in Fig. (2). Simulation were carried out on P4 computer, 1.6 GHz CPU with 2 GB RAM.

Model validation

In order to validate the one dimensional and two dimensional

models, the two models are written according to design and operating conditions for the industrial reactor that summarized in table (5). The modeling results are compared with the available experimental results as can shown in table (6) for output temperature, pressure and ethylbenzene conversion. For both two models the percentage error was small, but the two dimensional model gives lower error than one dimensional model, therefore both models could predict the behaviour of the fixed bed reactor well. Inspite the accuracy of two dimensional model, this model requires more data, correlations, effort and time to solve a complicated system of equations that represnt this model.

The two-models are basically used for the chemical reaction taking place in the non-ideal fixed bed reactor. With these models it is possible to predict the outlet temperature, pressure, concentrations, and then the conversion of a particular reactant taking part in the chemical reaction in the fixed bed reactor.

Results and Discussion

The ethylbenzene dehydrogenation is an endothermic and reversible reaction with an increase in the number of mole due to reaction. High equilibrium conversion can be achieved by a high temperature and a low ethylbenzene partial pressure. The main by products are benzene and toluene.

Ethylbenzene conversion is calculated using the definitions below.

$$\% \text{ Conversion} = \frac{F_{EB}^{0} - F_{EB}}{F_{EB}^{0}} \times 100 \quad \ldots\ldots (37)$$

Figures (3 to 12) show the one dimensional model results for ethylbenzene, styrene, hydrogen, benzene, ethylene, toluene methane, water, carbon monoxide, carbon dioxide respectively. Figures (13 - 22) show the two dimensional model results for ethylbenzene, styrene, hydrogen, benzene, ethylene, toluene methane, water, carbon monoxide, carbon dioxide.

Figures (23, 25 and 27) shows one dimensional model results for the temperature, pressure and ethylbenzene conversion profiles along the reactor length. Figures (24, 26 and 28) shows two dimensional model results for temperature, pressure and ethylbenzene conversion profiles along the reactor axis.

According to figures (23 and 24), the rate of decrease in reactor temperature is high initially and slow down with the reactor length. This is due to the fact that the main reaction (Eq. 4) is a reversible endothermic reaction. Therefore there is a proportion between the ethylbenzene conversion and the rate of temperature decreases along the length of the reactor. High initial temperature is required to achieve high conversion of ethyl benzene to styrene.

According to figures (25 and 26), the pressure in fixed bed reactor is drop linearly with reactor length and this is due to the fact that the total pressure drop in the reactor is about 0.08 bar which is less then 4% of the initial pressure in the reactor 2.4 bar.

Figures (13 to 22) proofs that two dimensional model is a very good tool to understand the conversion and selectivity of muti-reactions in fixed bed reactor.

In the case of two dimensional model there is no radial concentration and temperatue gradient due to boundary condition in the center and at the reactor wall are both for heat balance and for mass balance ($\frac{\partial T}{\partial r} = 0$ and $\frac{\partial C_i}{\partial r} = 0$).

The two dimensional program is un-useful to study optimization of fixed bed reactor due two resons as below:

1.The two dimensional model is highly non-linear comparing with one diemensional model.

2.The time required to operate the one dimensional program is approximately 10 % of time required to operate two dimensional program.

Conclusions

1. Both two models was successfully used for simulate industrial fixed bed reactor with multi-reaction to represent pressure, temperature and concentrations along the reactor.
2. The two dimensional model considers both axial and radial dispersion of heat and mass and consequently provides a good tool to understand the reactor performance. The two dimensional model can provide valuable additional information about temperature and concentration gradients in two dimension plane, and this is not available in a simple one-dimensional model.
3. The well known thermal behaviuor of exothermic reactions in fixed bed reactors could be predicted by the two dimensional model.
4. Ergun equation is suitable to represent the pressure drop in fixed bed reactor for both one dimension and two dimension models.

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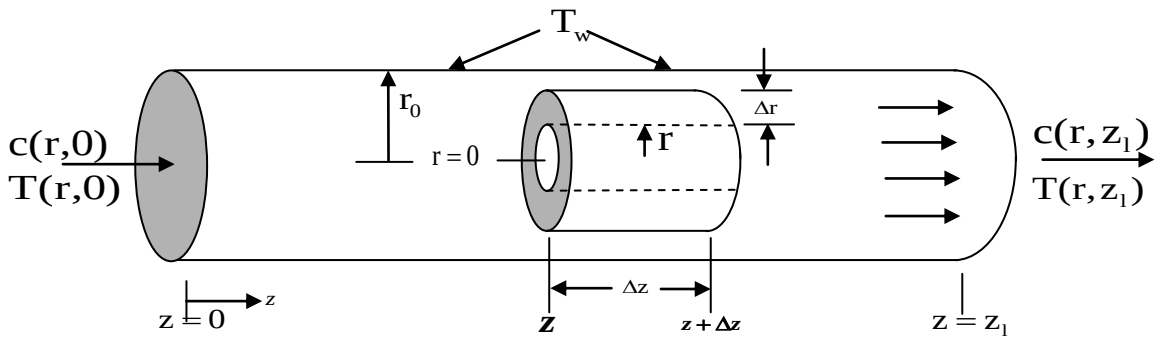

Figure (1) Cylindrical Shell of Thickness Δr and Length Δz in Fixed Bed Reactor

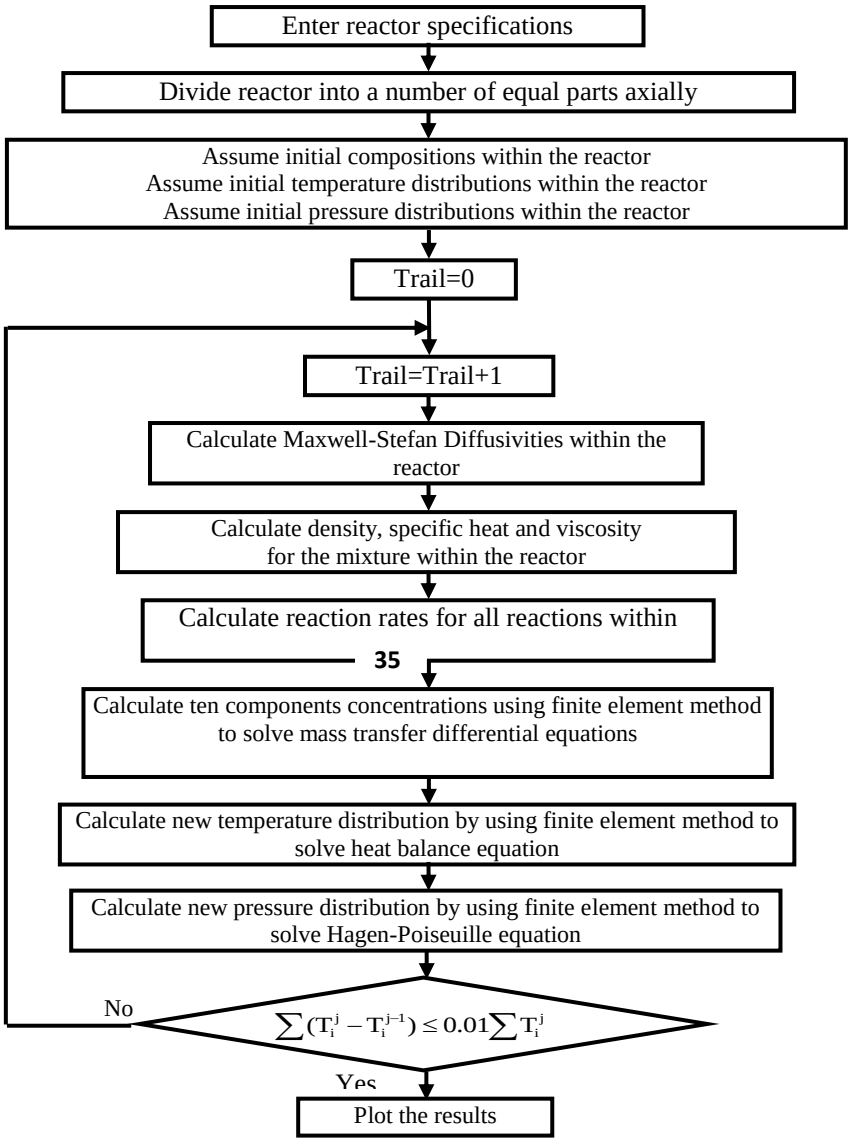

Fig. (2) Flow Chart for Fixed Bed Reactor Simulation Program

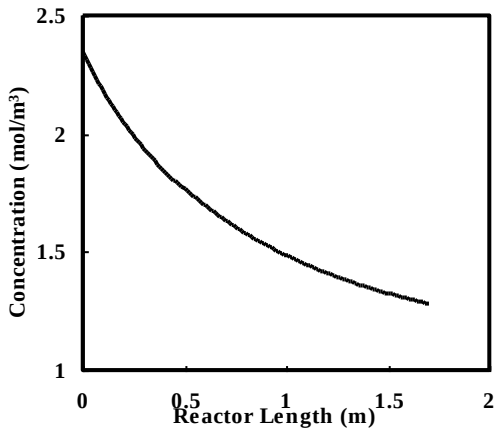

Fig. (3) Ethylbenzene concentration along the fixed bed reactor (one dimension)

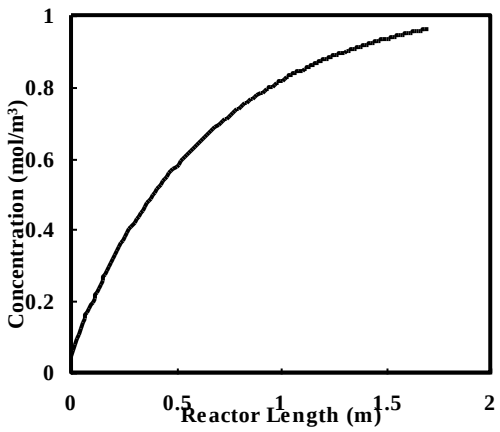

Fig. (4) Styrene concentration along the fixed bed reactor (one dimension)

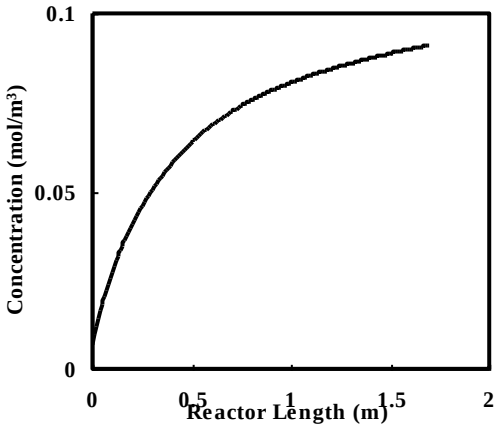

Fig. (5) Hydrogen concentration along the fixed bed reactor (one dimension)

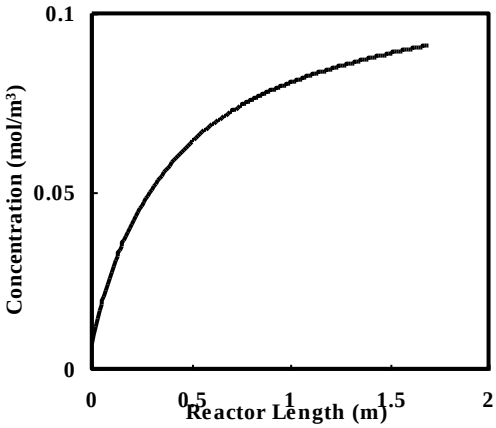

Fig. (6) Benzene concentration along the fixed bed reactor (one dimension)

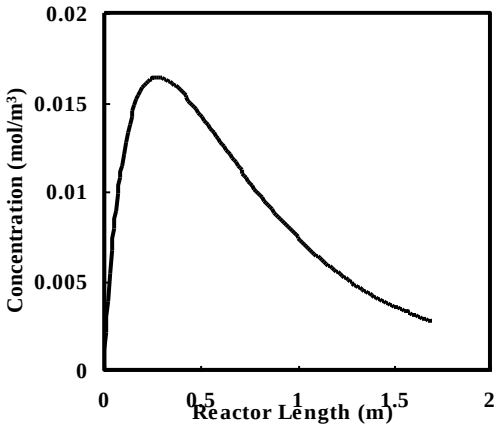

Fig. (7) Ethylene concentration along the fixed bed reactor (one dimension)

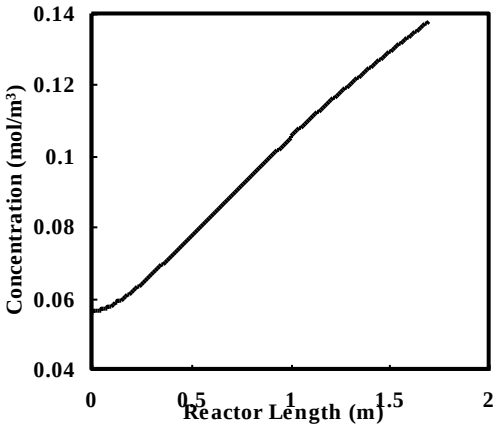

Fig. (8) Toluene concentration along the fixed bed reactor (one dimension)

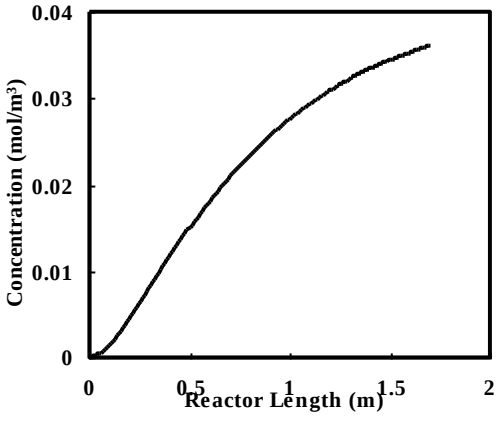

Fig. (9) Methane concentration along the fixed bed reactor (one dimension)

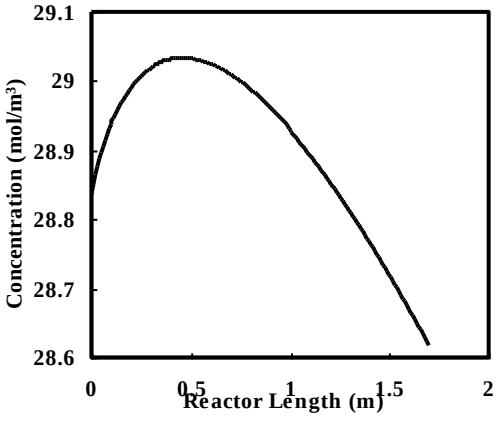

Fig. (10) Water concentration along the fixed bed reactor (one dimension)

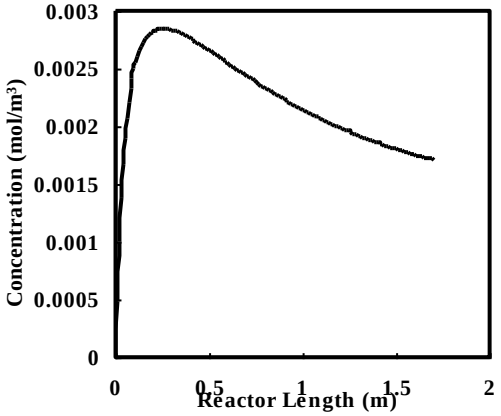

Fig. (11) Carbon monoxide concentration along the fixed bed reactor (one dimension)

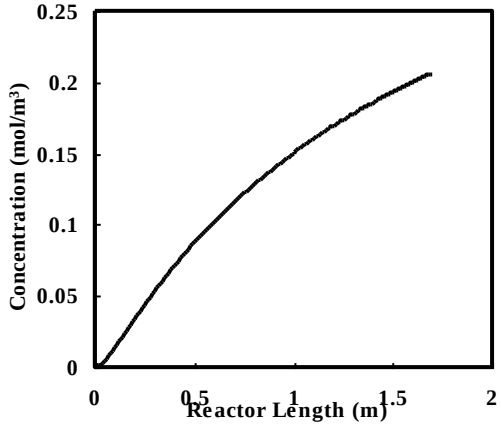

Fig. (12) Carbon dioxide concentration along the fixed bed reactor (one dimension)

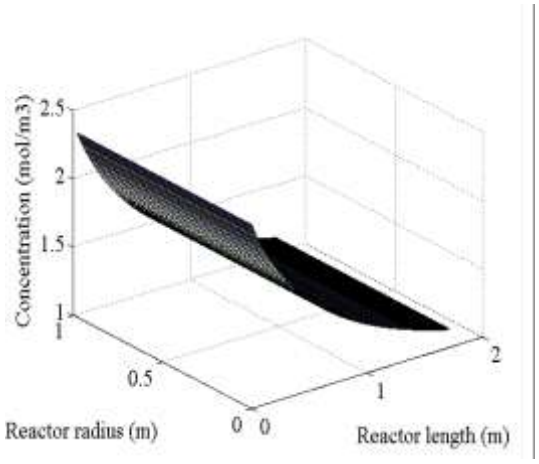

Fig. (13) Ethylbenzene concentration profile for fixed bed reactor (two dimension)

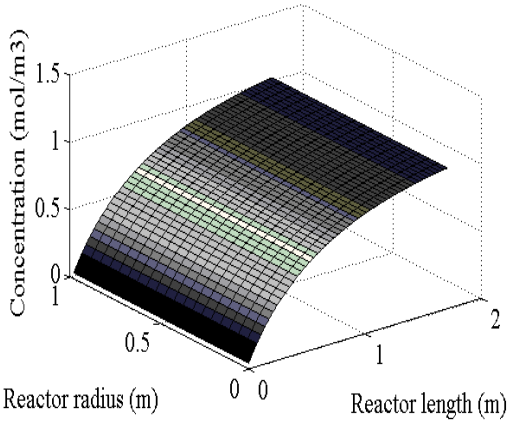

Fig. (14) Styrene concentration profile for fixed bed reactor (two dimension)

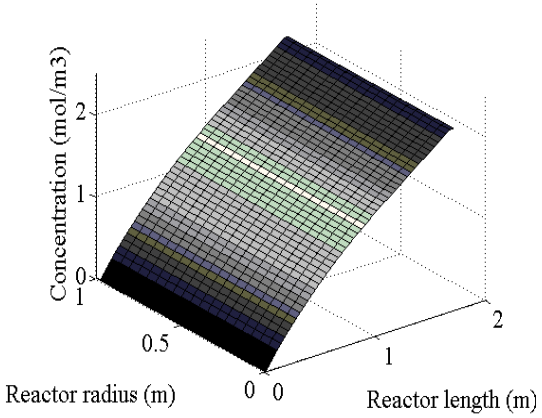

Fig. (15) Hydrogen concentration profile for fixed bed reactor (two dimension)

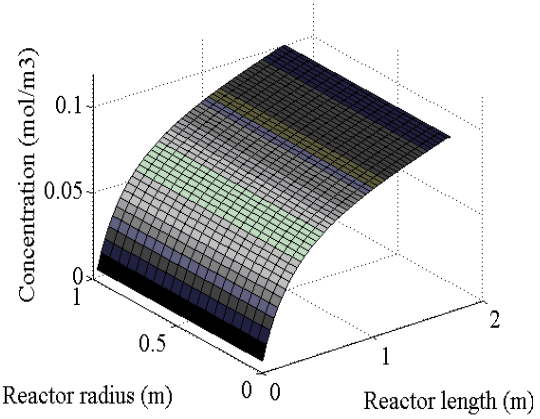

Fig. (16) Benzene concentration profile for fixed bed reactor (two dimension)

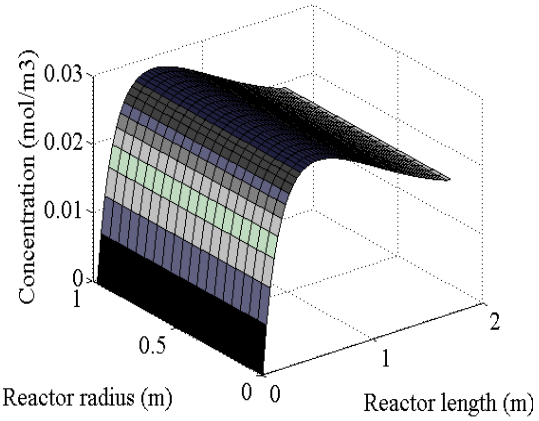

Fig. (17) Ethylene concentration profile for fixed bed reactor (two dimension)

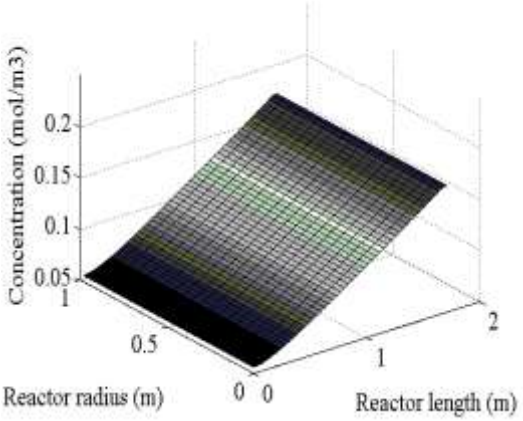

Fig. (18) Toluene concentration profile for fixed bed reactor (two dimension)

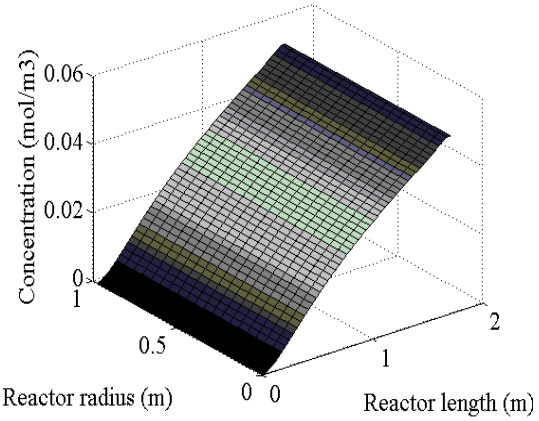

Fig. (19) Methane concentration profile for fixed bed reactor (two dimension)

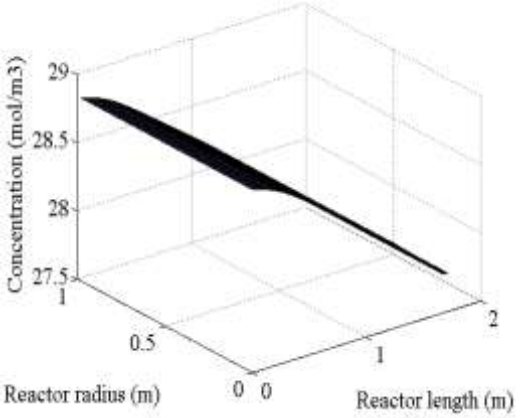

Fig. (20) Water concentration profile for fixed bed reactor (two dimension)

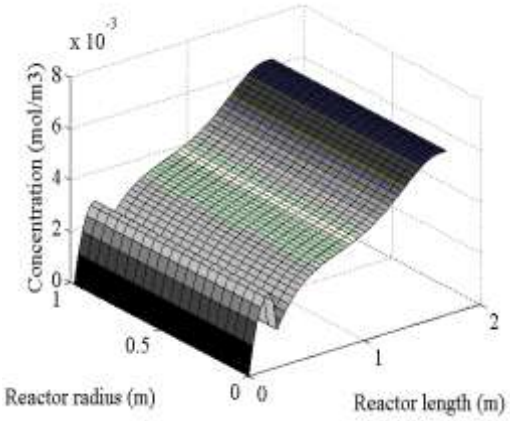

Fig. (21) Carbon monoxide concentration profile for fixed bed reactor (two dimension)

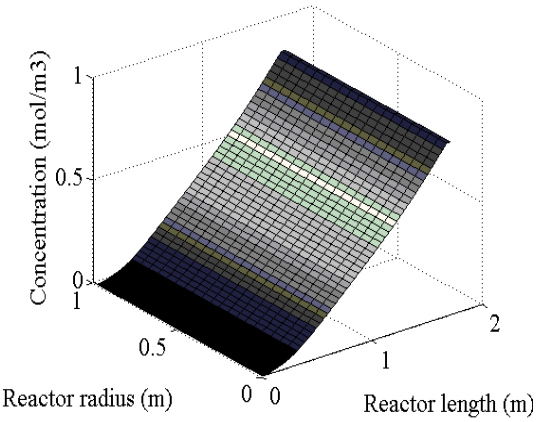

Fig. (22) Carbon dioxide concentration profile for fixed bed reactor (two dimension)

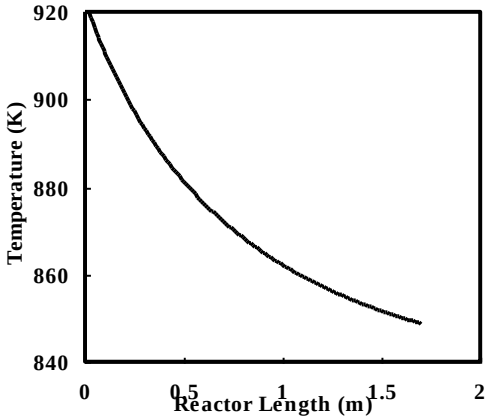

Fig. (23) Temperature variation along the fixed bed reactor (one dimension)

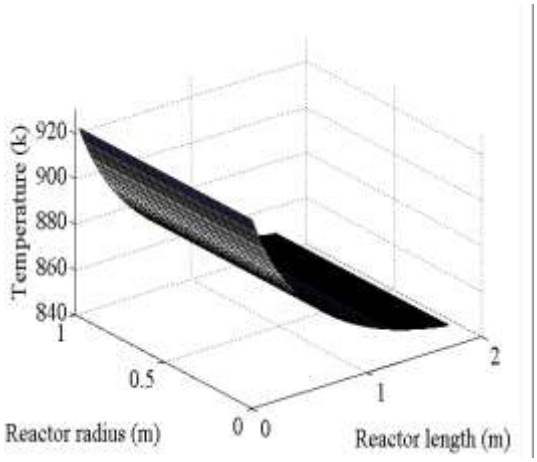

Fig. (24) Temperature variation along the fixed bed reactor (two dimension)

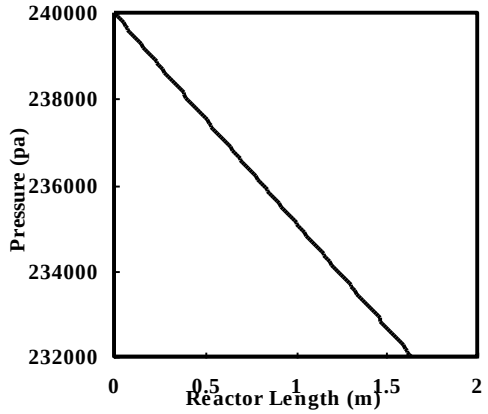

Fig. (25) Pressure variation along the fixed bed reactor (one dimension)

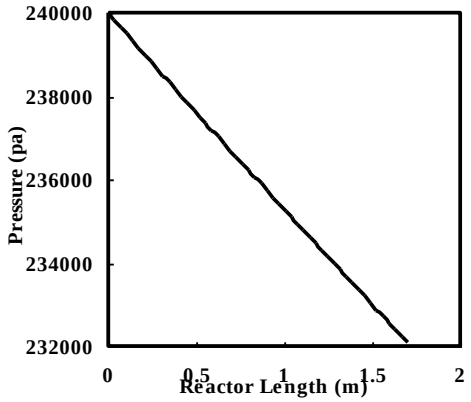

Fig. (26) Pressure variation along the fixed bed reactor (two dimension)

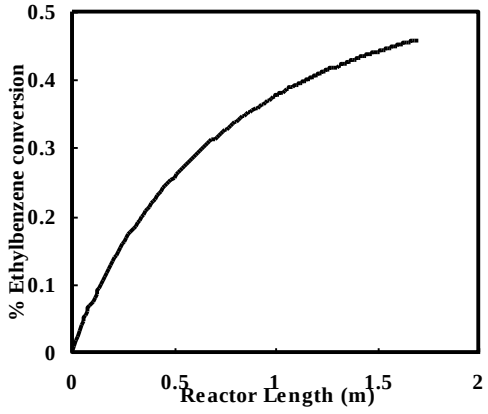

Fig. (27) Ethylbenzene conversion along the fixed bed reactor (one dimension)

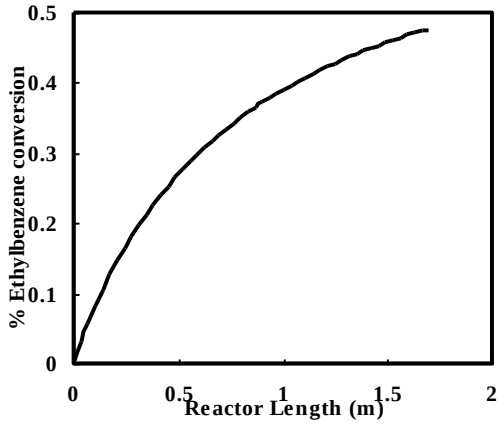

Fig. (28) Average ethylbenzene conversion along the fixed bed reactor (two dimension)

Table (1). Rate Constants for Reactions 4-9 [21]

	Rate Expression	Ej (KJ/Kmol)	Aj (-)
1	$r_1 = k_1(P_{EB} - P_{Sty}P_{H_2} / K_{Eq})$	90,981.4	- 0.0854
2	$r_2 = k_2 P_{EB}$	207,989.2	13.2392
3	$r_3 = k_3 P_{EB} P_{H_2}$	915,15.3	0.2961
4	$r_4 = k_4 P_{H_2O} P_{Ethane}^{0.5}$	103,996.7	- 0.0724
5	$r_5 = k_5 P_{steam} P_{Methane}$	65,723.3	- 2.9344
6	$r_6 = k_6 (P/T^3) P_{Steam} P_{CO}$	73,628.4	21.2402
$k_j = \exp(A_j - E_j / RT)$			
$K_{Eq} = \exp[(-122725 + 126.3T + 0.002194T^2)/RT]$			

Table (2) Coefficients of Viscosity Polynomial [27]

Species	A [N/s.m^2]	B×10^1 [N/	C×10^5 [N/	Mw [gm/mol]
Ethylbenzene	-4.267	2.4735	-5.4264	106.168
Styrene	-10.035	2.5191	-3.7932	104.151
Benzene	-0.151	2.5706	-0.89797	78.114
Toluene	1.787	2.3566	-0.93508	92.141
Ethylene	-3.985	3.8726	-11.227	28.054
Methane	3.844	4.0112	-14.303	16.043
Water	-36.826	4.29	-1.62	18.015
Carbon	23.811	5.3944	-15.411	28.010
Carbon dioxide	11.811	4.9838	-10.851	44.010
Hydrogen	27.758	2.12	-3.28	2.016

$$\mu = A + BT + CT^2 \qquad (N/s.m^2)$$

Table (3) Coefficients of Heat Capacaity Polynomial [26]

Species	A [cal/mol.^{o}k]	B×10^2[cal/mol.	C×10^5[cal/mol.	D×10^8[cal/mol.
Ethylbenzene	-10.294	16.89	-0.1149	3.107
Styrene	-6.747	14.71	-9.609	2.373
Benzene	-8.101	11.33	-7.206	1.703
Toluene	-5.817	12.24	-6.605	1.173
Ethylene	0.909	3.740	-1.994	0.4192
Methane	4.598	1.245	0.2860	-0.2703
Water	7.701	0.04595	0.2521	-0.0859
Carbon	7.373	-0.307	0.6662	-0.3037
Carbon dioxide	4.728	1.754	1.338	0.4097
Hydrogen	6.483	2.215	-0.3298	0.1826

$Cp = A + BT + CT^2 + DT^2$ (cal/mol.^{o}k)

Table (4) Coefficients of Heat Conductivity Polynomial [27]

Species	$A\times10^{2}$[w/m.^{o}k]	$B\times10^{4}$ [w/m.^{o}k^{2}]	$C\times10^{8}$ [w/m.^{o}k^{3}]
Ethylbenzene	-0.797	0.40572	6.7289
Styrene	-0.712	0.45538	3.9529
Benzene	-0. 565	0.34493	6.9298
Toluene	-0. 776	0.44905	6.4514
Ethylene	-0. 123	0.36219	12.459
Methane	-0. 935	1.4028	3.318
Water	0.053	0.47093	4.9551
Carbon monoxide	0. 158	0.82511	-1.9081
Carbon dioxide	-1.200	1.0208	-2.2403
Hydrogen	3.951	4.5918	-6.4933

$k = A + BT + CT^2$ (w/m.k)

Table (5) Design and Operating Conditions for the Industrial Reactor [5, 9].

Reactor diameter	1.95 m
Catalyst bed depth	1.7 m
Catalyst bulk desnsity	2146 kg/m^3
Catalyst particle diameter	0.0047m
Bed void fraction	0.445
Catalyst composition	62% Fe_2O_3, 36% K_2CO_3, 2% Cr_2O_3
Inlet pressure	2.4 bar
Inlet temperature	922.59 K
Ethyl benzene in the feed	36.87 kmol/h
Styrene in the feed*	0.67 kmol/h
Benzene in the feed*	0.11 kmol/h
Toluene in the feed*	0.88 kmol/h
Steam	453.1 kmol/h
* These three components are present as impurities in the ethyl benzene feed.	

Table (6). Comparison of the Simulation Results with the Industrial Data [5, 9].

Quantity at reactor exit	Industrial data	1 D model		2 D model	
		results	% Error	results	%Error
Exit temperature, K	850.0	848.7748	0.140	849.7701	0.0270
Exit Pressure, bar	2.32	2.3172	0.120	2.3209	-0.0388
Ethyl benzene conversion, %	47.25	45.83	3.010	47.46	-0.4400