Non-Isothermal Modeling of Ethane Thermal Cracker

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Extended Abstract

The production of olefins through cracking has been the backbone for the explosive growth of petrochemical and allied industries witnessed in the last few decades. Ethylene production has been the single major building block for this growth of industry. Conventionally, petroleum based feedstocks like naphtha, refinery gas, gas oils etc. have been utilized in the crackers. Even natural gas has been used for ethylene production. In thermal cracking, there is a high degree of flexibility in terms of feeds that can be used compared to catalytic cracking. This is so due to the fact that feed pretreatment is a prerequisite in catalytic systems to take care of the poisons and inhibitors. In addition, the compatibility of feed and the catalyst is required unlike the case of thermal cracking, where no such constraint on operation is there. The catalytic process has found favour with the industry recently due to better control on product distribution and lower temperatures but the simplicity of thermal cracking operation cannot be overlooked. The latter factor gives thermal cracking a definite edge over catalytic cracking. The presence of metals and asphaltenic material in the residues is a serious factor for using catalytic process. The delayed coking process to handle vacuum and atmospheric residues is a controlled thermal cracking such that the reactions are delayed suitably by operating at high velocities. To deal with the heavy stocks, vis-breaking for viscosity reduction is another application area in the refineries utilizing thermal cracking. The concept of thermal cracking has found application in the field of environmental pollution control to deal with plastic wastes with recovery of some useful chemicals.

The thermal cracker consists of long empty tubes (vertical) embedded in the radiation chamber of a furnace. As the process of thermal cracking is an endothermic one, the heat is supplied to the reactor tubes through the walls of the tubes from the furnace. The heat available at the reactor wall is transferred in the radial direction to the reaction mass. Assuming circumferential uniformity in the heat supply, non-isothermal conditions in radial and axial directions are encountered. This type of temperature variation results in the variation of reaction rates at the various locations radial as well as axial. Thus, concentration and temperature gradients shall exist in both the directions. In literature, the various modeling studies available are mostly based on 1-dimensional model, assuming plug flow conditions [Belohlav et.al 2003; Niaei et.al, 2004;Pant and Kunzru, 1996; Ramana Rao et.al,1988]. The model equations for the mass, energy and momentum are postulated in form of ODEs, neglecting the lateral gradients. The results depict only the axial variation assuming complete lateral mixing.

Sundaram and Froment [1979] have compared one-dimensional model to a two-dimensional model for pipe reactor with a single molecular reaction. The existence of concentration and temperature profiles in both the laminar and turbulent flow regimes has been reported. Also, it has been established that the use of an average Nusselt number from the 2-dimensional model improves the predictions of a 1-dimensional model. In another study

[Sundaram and Froment, 1980], the ethane cracker has been modeled using 2-dimensional approach under turbulent conditions for varying reactor wall temperature. It is demonstrated that the 2-dimensional approach leads to better predictions compared to 1-dimensional model. The projected product yields for some species at the reactor outlet are found to be in agreement with experimental data. The product distribution within the reactor has not been reported. Most of the reported studies in thermal cracker modeling rely on 1-dimensional model for it's obvious simplicity and the lateral gradients are disregarded. The 2-dimensional model has not been widely exploited although it is a better representation of the system.

In the present work, a 2-dimensional model for ethane cracking is established and results are simulated with an aim of obtaining the product distribution in the reactor and showing the effect of various operational conditions. Based upon a molecular reaction scheme proposed by Sundaram and Froment [1977] for ethane cracking, the model predicts the concentrations of all the species involved and temperature. The concentrations of all the species are predicted in axial and radial directions. In literature only the variation of ethane is reported in both the directions. The parameters for the thermal cracker operation like reactor pipe radius, wall temperature etc. influence the reactor behaviour. The effect of variation in these parameters on the product distribution, conversion and temperature profiles has been studied.

Model Development

Thermal cracker is essentially a tubular system, the walls of which are supplied with heat. The temperature at the wall is highest compared to other positions in a cross section. The resultant difference in reaction rates leads to the radial and axial concentration and temperature gradients. Mathematically, this type of effect can be described by partial differential equations.

Kinetic Mechanism

The molecular reaction scheme as proposed by Sundaram and Froment [1977] for ethane cracking is used. The main reactions, which are responsible for ethane decomposition into ethylene in terms of free radicals are as given below:

$$C_2H_6 + H^* \longrightarrow C_2H_5^* + H_2$$

$$C_2H_5^* \longrightarrow C_2H_4 + H^*$$

These two radical reactions are combined to yield the first molecular reaction for ethane pyrolysis. Similarly, other reactions have been proposed. All the reactions are assumed to be elementary except for the second reaction. The molecular reaction scheme is as follows:

$$C_2H_6 \underset{k_2}{\overset{k_1}{\rightleftarrows}} C_2H_4 + H_2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \Delta H_1$$

$$2C_2H_6 \xrightarrow{k_3} C_3H_8 + CH_4 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \Delta H_2$$

$$C_3H_6 \underset{k_5}{\overset{k_4}{\rightleftarrows}} C_2H_2 + CH_4 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \Delta H_3$$

$$C_2H_4 + C_2H_2 \xrightarrow{k_6} C_4H_6 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \Delta H_4$$

$$C_2H_4 + C_2H_6 \xrightarrow{k_7} C_3H_6 + CH_4 \ldots\ldots\ldots\ldots\ldots\ldots \Delta H_5 \qquad (1)$$

2-Dimensional model

In the proposed model the flow is assumed to be laminar under steady state conditions. The wall temperature is maintained constant. Also, it is assumed that the axial convective flow of mass and energy are dominant compared to the axial diffusive flow i.e. the latter terms are negligible. In the pipe reactor, the angular gradients are neglected. The necessary mass balances for the various species and energy balance equations are established.

The mass balance for the i-th species takes the form:

$$\frac{D_{mi}}{r}\frac{\partial}{\partial r}\left[r\rho_f\frac{\partial(C_i/\rho_f)}{\partial r}\right]-\rho_f u_m\left[1-\frac{r^2}{R^2}\right]\frac{\partial(C_i/\rho_f)}{\partial z}-(-r_i)=0 \qquad (2)$$

where i= species C_2H_6,C_2H_4…..

For each of the species a rate of dissociation can be written. For ethane the rate of dissociation is given by

$$-r_{C_2H_6}=k_1[C_2H_6]-k_2[C_2H_4][H_2]+k_3[C_2H_6]+k_7[C_2H_6][C_2H_4] \qquad (3)$$

The rate constant for i-th reaction, is given by Arrhenius Law as

$$k_i=k_{i0}\exp\left[-\frac{E_i}{R(T+273)}\right] \qquad (4)$$

The energy balance, assuming endothermic reaction, is

$$\frac{k_{th}}{r}\frac{\partial}{\partial r}\left[r\frac{\partial T}{\partial r}\right]-\rho_f C_p u_m\left[1-\frac{r^2}{R^2}\right]\frac{\partial T}{\partial z}-\sum_i \Delta H_{ri}(-r_i)=0 \qquad (5)$$

The boundary conditions for this model are

1.At axis, $0 \le z \le L$, $\frac{\partial C_i/\rho_f}{\partial r}=0,\frac{\partial T}{\partial r}=0$ (6.1)

2.At wall, $0 \le z \le L$, $\frac{\partial C_i/\rho_f}{\partial r}=0$,$T=T_w$ (6.2)

3.At the reactor entrance

$0 \le r < R$, $z=0$, $[C_2H_6]=[C_2H_6]_0$, $T=T_0$ and all other product species are absent. (6.3)

Model Solution and Evaluation

For all the eight species, equations 2 and 6 are established. The resulting set of equations present the case of strong coupling among the nine PDEs involved. These coupled equations are solved by finite difference numerical method. The backward implicit finite difference numerical scheme has been used to solve these nine coupled PDEs as reported by Srivastava [1983]. The mass balance and energy balance can be represented as **A.X**=**B** in matrix notation. To economize on computing time and space, the tridiagonal banded coefficient matrix **A** of M*M dimension was transformed through a technique to yield an equivalent M*3 matrix [Srivastava 1983]. The resulting equations were solved using Srivastava's algorithm [Srivastava 1983]. The model predictions were compared to analytical results for the Graetz problem by considering the energy balance alone without chemical reaction. The model predictions and analytical results have shown a remarkable consistency.

Results and Discussion

The 2-dimensional reactor model is used to predict product distribution and temperature profiles. Assuming an ethane to nitrogen ratio of 4:1, reactor dimensions (r=1cm, L=120cm), the model is simulated. Figures 1-5 are the graphical representation of the various results obtained for different conditions of operation. Fig.1a demonstrates the effect of variation in conditions in the wall zone compared to the region near the axis. At z=0.60 m, the concentration of ethane reduces on moving away from the axis towards the wall; whereas that of products show a decrease towards the axis. For ethylene, the concentration changes from 1.5 to 3.95 gmol/kg in moving radially from the centre towards the wall. The concentration profile for hydrogen is almost flat due to it's high diffusivity. Radial temperature profiles at

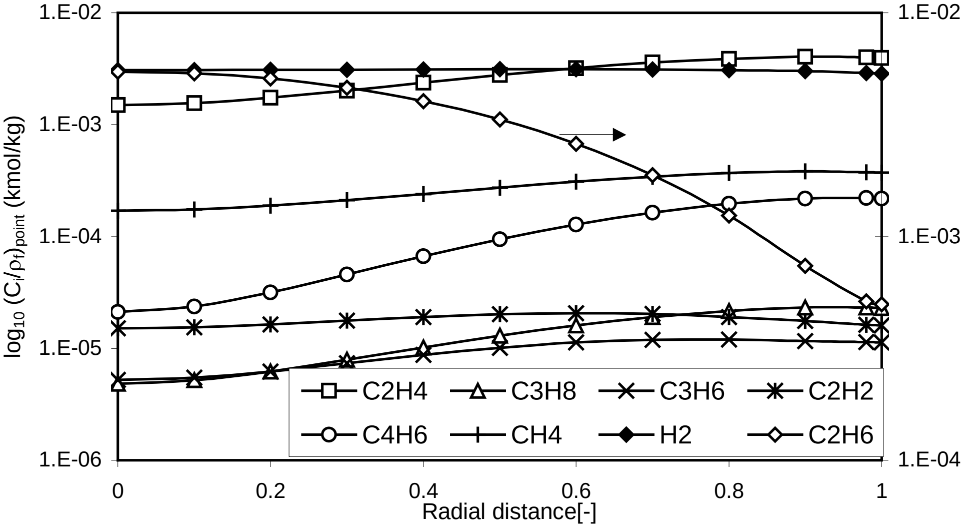

Fig.1a: Radial concentration profiles(r=0.01m,T_w=1000°C)

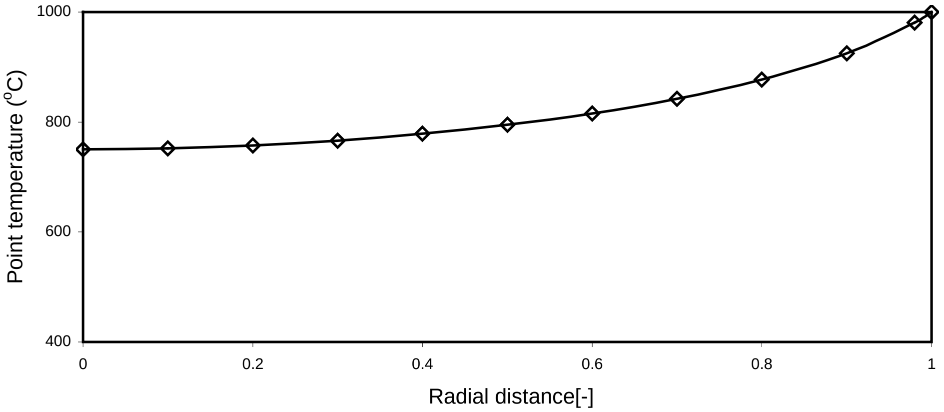

Fig.1b: Radial temperature profile(r=0.01m,T_w=1000°C)

z=0.60 are depicted in Fig.1b. The temperature in the central zone is lower compared to that near the wall, demonstrating the existence of radial temperature variations resulting in variation of reaction rates.

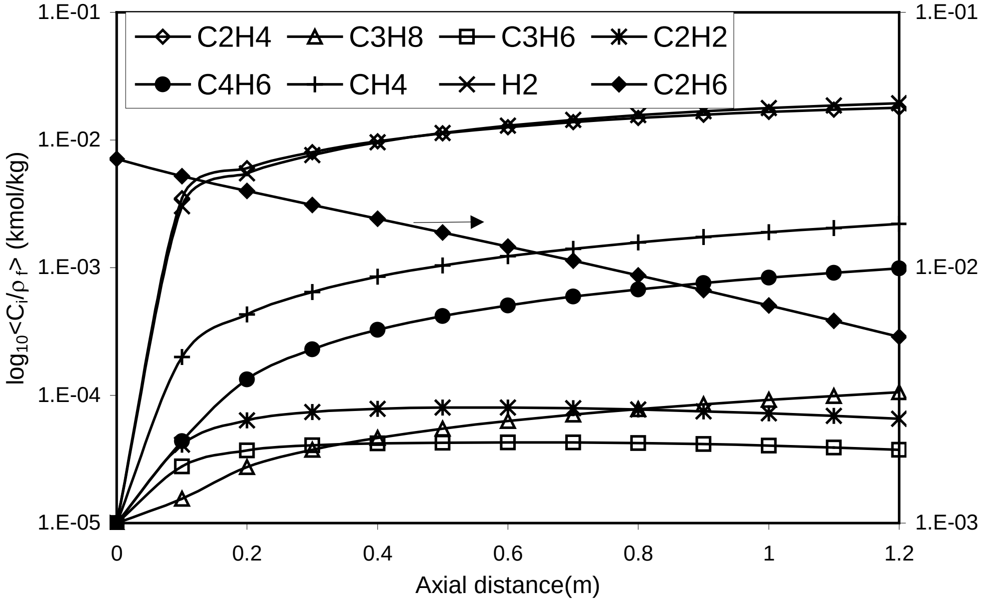

Fig. 2a:Axial concentration profiles(r=0.01m, T_w =1000^{o}C)

Figures 2a and 2b show the axial average concentration and temperature profiles. The results show that ethane conversion increases up to 80% in moving along the reactor length. On the other hand the concentration of product species increase down the reactor, the concentrations of propylene and acetylene are very low in the reactor. A maximum value is achieved in the concentrations of propylene and acetylene. This maximum is due to the relative amount of dissociation rate and formation rate for the reactions in which they are involved. As per the simulated results, the reaction mass gets heated up from 600 ^{o}C at the entrance to an average value of 868.1 ^{o}C at the exit (Fig. 2b). This temperature rise despite heat consumption by reaction is found due to the maintenance of wall temperature constant.

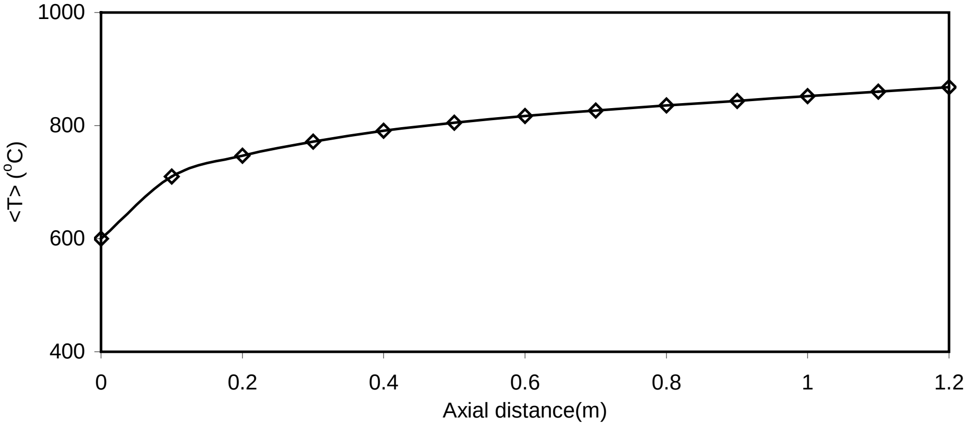

Fig. 2b:Axial temperature profile(r=0.01m, T_w =1000^{o}C)

The operational or design parameters of the reactor influence the extent of reaction and product distribution in addition to the effect of physical properties of the system. The effect of operational aspects of the pipe reactor is studied by simulating the model predictions under various conditions. The tube radius, flow rate and wall temperature have been selected as the parameters to be studied. The effect of variation in these parameters on the profiles existing in the reactor is obtained from the model, which depict the dependence of these profiles on the parameters investigated.

Effect of wall temperature

The effect of change in the wall temperature is presented in terms of axial profiles in Figures 3a and 3b. The cracker wall temperature is varied from 900 – 1100^{o}C. With an increase in the wall temperature the endothermic process is favoured, giving higher conversion of ethane with a corresponding increase in product species concentrations. An increase in T_w results in increase in process average temperature at any axial position (Fig.3b). Although the higher wall temperature dictates higher heat consumption by reaction, the maintenance of constant wall temperature dominates in terms of heat supplied compared to the heat utilized by the reaction.

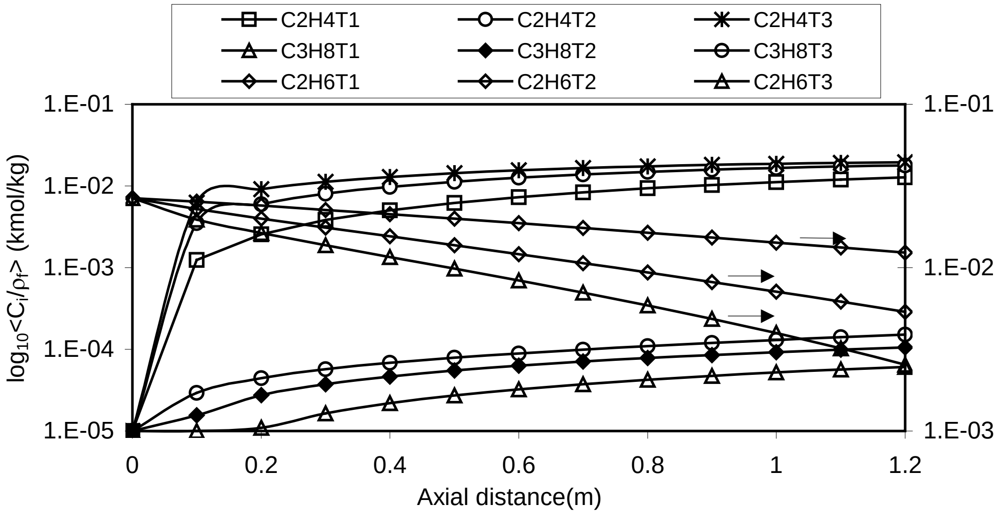

Fig. 3a:Effect of wall temperature on axial concentration profiles
(r=0.01m, T_{w1}=900^{o}C, T_{w2}=1000^{o}C , T_{w3}=1100^{o}C)

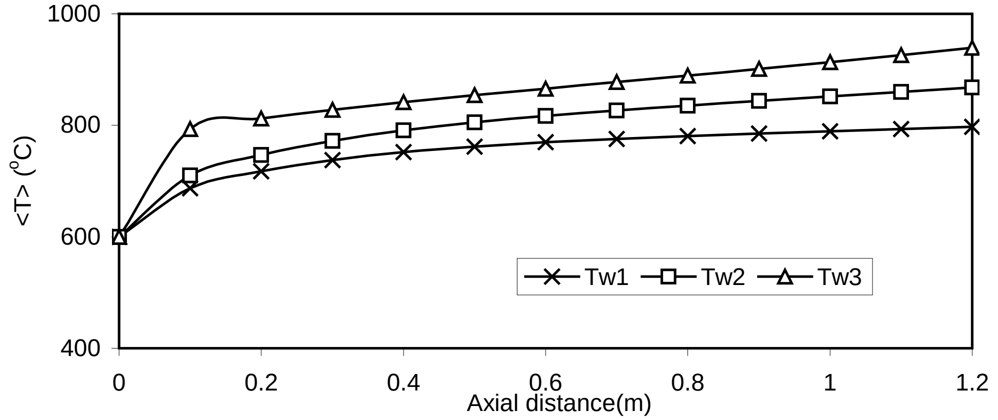

Fig. 3b:Effect of wall temperature on axial temperature profiles
(r=0.01m, T_{w1}=900^{o}C, T_{w2}=1000^{o}C , T_{w3}=1100^{o}C)

Effect of tube radius

The reactor tube radius for the reactor operation is varied in the range 0.5cm to 1.25m. The effect on average concentration and temperature profiles due to this variation is depicted in Figures 4a and 4b respectively. At any axial position, as the tube radius is decreased, a lower extent of conversion is observed with a corresponding decrease in the concentrations of other species (Fig.4a) due to the decrease in the residence time. As the tube radius increases, at any axial position, the temperature gain shows an increase (Fig. 4b). The residence time increases for increase in tube radius and the wall temperature is being maintained though more reaction is there, consuming more of heat. The former factors dominate leading to more temperature gain with increasing tube radius.

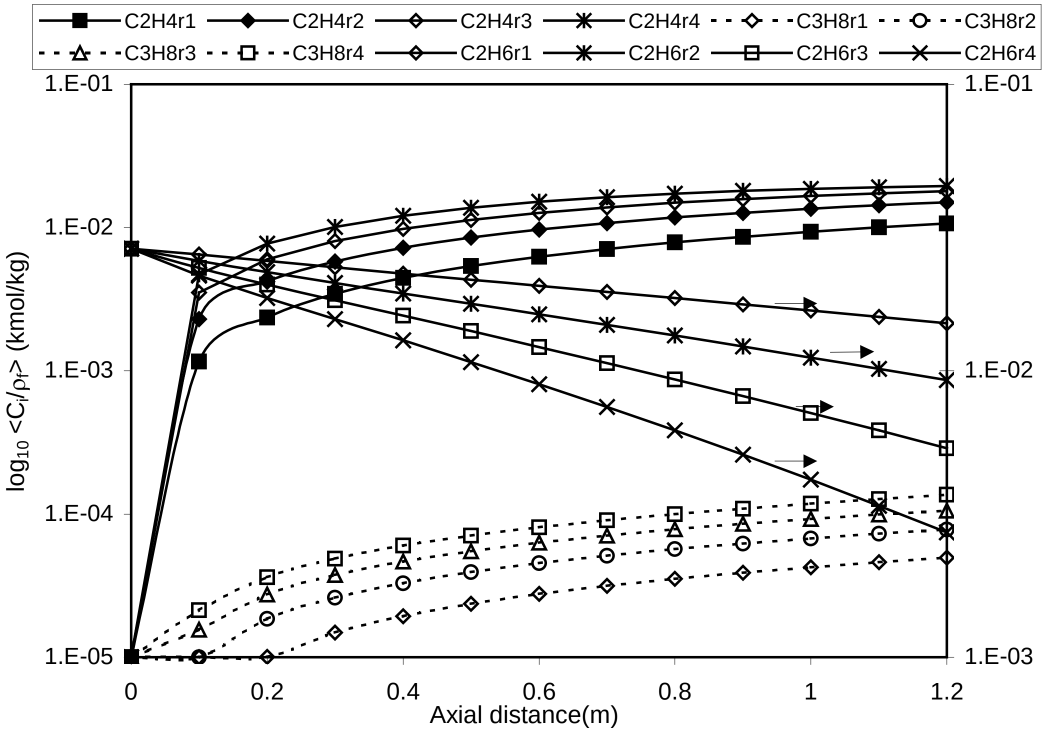

Fig. 4a:Effect of tube radius on axial concentration profiles
(T_w=1000^{o}C,r_1=0.5cm,r_2=0.75cm,r_3=1cm,r_4=1.25cm)

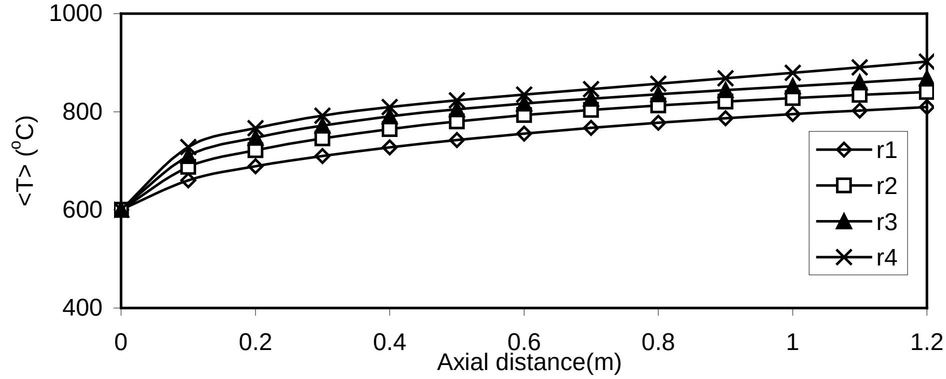

Fig. 4b: Effect of tube radius on axial temperature profiles
(T_w=1000^{o}C,r_1=0.5cm,r_2=0.75cm,r_3=1cm,r_4=1.25cm)

Effect of flow rate

The mass flow rate is varied up to double the base case and the effect of this change is depicted in Fig. 5a for axial concentration profiles and Fig. 5b for temperature. As is clear from Fig. 5a, an increase in flow rate results in a lower conversion for ethane and thus lower yields for the product species. The lowering of residence time is causing this type of dependence. The effect of increase in mass flow rate on axial temperature profiles (Fig. 5b) is

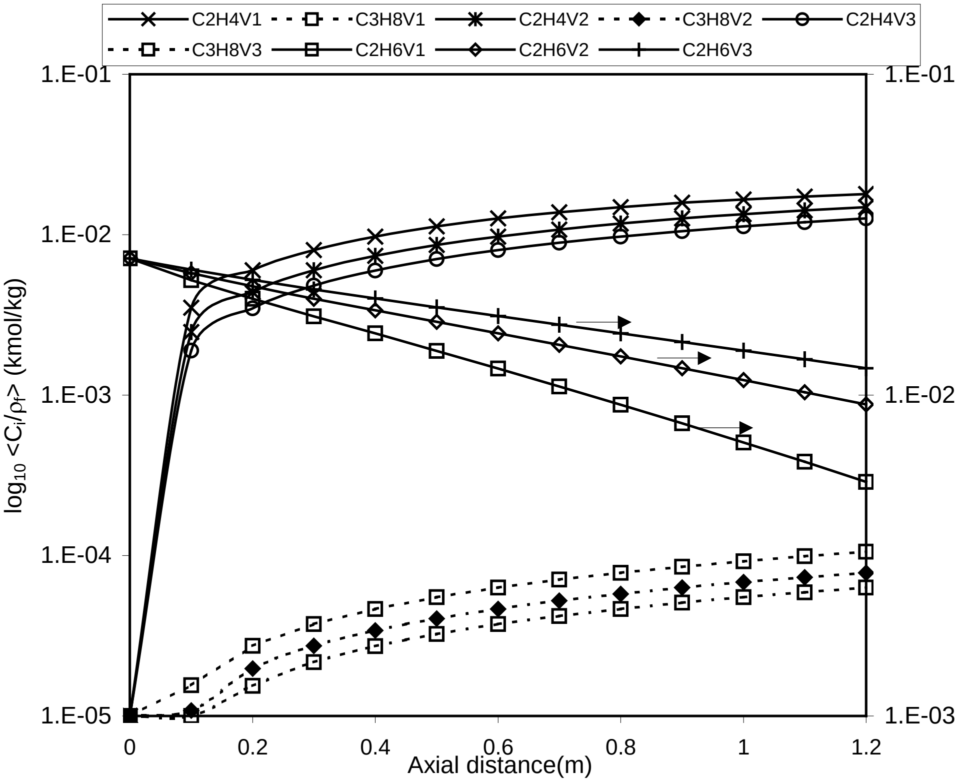

Fig. 5a:Effect of flow rate on axial concentration profiles
(r=0.01m, T_w =1000^{o}C,V_3:V_1=2, V_2:V_1=1.5)

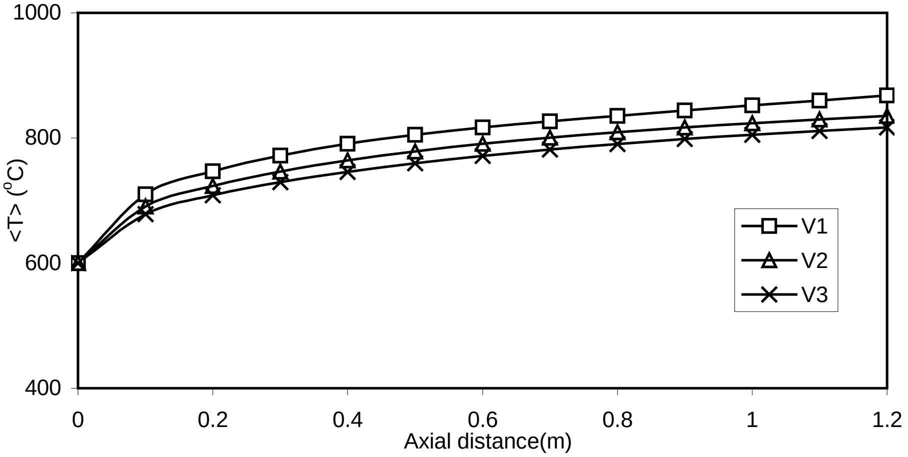

Fig. 5b:Effect of flow rate on axial temperature profiles
(r=0.01m, T_w =1000^{o}C,V_3:V_1=2, V_2:V_1=1.5)

that an increase in flow rate results in lowering of temperature at any axial position. The explanation is similar to that in tube radius case.

Conclusions

The thermal cracking of ethane has been done by proposing a two dimensional model considering the lateral gradients. The radial temperature and concentration profiles predicted by the model are as per expectations as they are set up under the influence of radial diffusion and conduction effects. The high diffusivity of hydrogen results in almost a flat radial profile for hydrogen concentration. The simulated product distribution inside the reactor is averaged over a cross section at any axial position and it is observed that the concentrations of acetylene and propylene are the least out of the various product species. The concentrations of these two components also pass through a maximum within the reactor. The effect of the operational parameters, namely tube radius, wall temperature and flow rate has also been simulated. As per the predictions, the lower flow rate, higher tube radius and higher wall temperature leads to higher conversion of ethane.

Nomenclature

C_i	conc of species i , (kmol/m^3)
C_{i0}	conc of species i at entrance of reactor, (kmol/m^3)
C_{AVG}	average concentration , (kmol/m^3)
$<Ci/\rho_f>$	average concentration , (kmol/kg)
C_p	specific heat, (kJ/kg^{o}C)
$D_{m,i}$	diffusivity of species i, (m^2/s)
E_i	activation energy, (kJ/mol)
$\Delta H_{r,i}$	heat of reaction i , (kJ/mol)
k_{th}	thermal conductivity, (W/m ^{o}C)
k_i	reaction rate constant of reaction i, (conc $^{1-n}$/s)
k_{i0}	frequency factor, (conc $^{1-n}$/s)
L	length of reactor, (m)
r	radius(local),radial coordinate, (m)
R	pipe radius, (m)
T	process temperature, (^{o}C)
T_0	inlet temperature, (^{o}C)
T_w	wall temperature, (^{o}C)
$<T>$	average temperature, (^{o}C)
u_m	max. velocity, (m/s)
z	reactor axial dimension, (m)

Greek symbols

ρ_f	density, (kg/m^3)

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