

Simulation and Analysis of Ethane Cracking Process

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Abstract: The olefins are widely produced using thermal cracking of light hydrocarbons such as ethane, propane, n-butane and their mixtures. A mixture of inert steam and hydrocarbon feed stocks are entered into coiled tubular reactors with high temperatures and short residence times. Ethylene is produced in the largest volume among the important base petrochemicals that forms the building blocks of the petrochemical industry. Thus any improvement in the process of ethylene production may enhance the industrial economic output. Present work focuses on the simulation of ethylene production plant. An industrial reactor unit using ethane as a feedstock is simulated for the molecular reaction scheme with 8 components and 5 reactions. A detailed free-radical mechanism for the reaction kinetics coupled with material, energy and momentum balances of the reactant-product flow along the reactor is considered. A detailed simulation study is carried out and the model predictions are compared with the industrial data and the data reported in the literature. Model predicted results and an industrial data are matching in terms of concentrations of species but have some deviation in terms of temperature and pressures predictions. However, profiles of temperature and concentration, along the length of reactor are matching. The effects of feed temperature and the internal diameter of tube (reactor) on the conversion of ethylene have been studied. The effect of these parameters on other specific issues such as the tube outlet temperature, tube outlet pressure, exit flow rates of reactants and products such as methane, ethane, ethylene, and propylene, etc., is also reported. Such a study may be extended to carry out improved kinetic parametric estimation (using a better model) and multi-objective optimization study of important process design decisions.

Keywords: Cracking; Modeling and simulation; Free-radical mechanisms; Reaction engineering; Process design

Introduction

Ethylene is usually produced through the steam cracking of feed stocks such as ethane, naphtha, or gas oil. The choice of feed stock is an important economic decision as it influences other costs as well. Subject to availability, ethane is probably the best feedstock, as it has higher yield and selectivity of ethylene than heavier feed stocks and its processing is relatively simple, involving lower capital costs. Steam-cracking is an endothermic process leading to the breaking up of large molecules into smaller ones. The cracking process is carried out in long tubular reactors, known as radiant tubes, which are placed vertically in a large, rectangular gas-fired furnace. The furnace consists of convection and radiation sections, where the feedstock first enters the convection section so that the hot stack gas preheats the feed before it enters the radiation section. Typical inlet temperatures to the radiant tube range from 500 to 800 °C. At an intermediate point in the convection section, steam is introduced and is preheated together with the feedstock. Steam lowers the partial pressure of high-molecular mass aromatics, reducing condensation reactions; in addition, it contributes to the partial removal of coke in the tubes. The radiant coil is directly heated by the burners, leading the process gas to the cracking temperature, which ranges from 700 to 900 °C. The temperature at the outlet of the radiant coil typically ranges from 775 to 885 °C. The reactor effluent is quickly quenched to prevent further reaction; compressed; and sent to a separation unit for the recovery of ethylene and other products such as methane, ethane, propane, propylene, butylenes, and gasoline [1].

An industrial reactor unit using ethane as the feedstock was modeled [1], assuming a detailed free-radical mechanism for the reaction kinetics coupled with material, energy, and momentum balances of the reactant-product flow along the reactor.

Reaction Mechanism and Modeling of Steam Cracker

The reaction mechanism of steam cracking of hydrocarbons to form ethylene can be formulated in different ways, namely, according to overall, molecular, and free-radical mechanisms, of which the last is the most detailed and perhaps the most accurate. Froment and his group [2, 3] proposed molecular schemes approximating the free-radical nature of ethane cracking, where kinetic parameters were estimated on the basis of pilot-plant data. These models are easier to solve because they lead to a set of non-stiff differential equations, whereas the free-radical mechanism leads to stiff differential equations that are difficult to solve. Sundaram and Froment [4] developed a free-radical scheme for ethane cracking, where 49 reactions were proposed and products heavier than C_5H_{10} , whose yields are usually very small, were lumped together as the single component C_{5+} to simplify the reaction scheme. Kinetic parameters were mainly obtained through trial and error and by fitting pilot-plant data. Other free-radical schemes have also been proposed by several authors, using fewer reactions. Tarafder et al. [1] evaluated several reaction schemes for ethane cracking, including the molecular and the free-radical schemes by Sundaram and Froment [5], and concluded that the free-radical mechanism of Sundaram and Froment [4] provides more accurate predictions. The results obtained in this study also found the same observation that model proposed by Sundaram and Froment [3] does not give accurate predictions. However, in order compare both the model output, we started with model proposed by Sundaram and Froment [3].

Table: 1. Reaction Scheme for Ethane Cracking [3]

Reaction	A (sec-1) or (l./mol sec)	E (kcal/kmol)
$C_2H_6 \xrightleftharpoons{k_1} C_2H_4 + H_2$	4.65×10^{13}	65,210
$2C_2H_6 \xrightarrow{k_2} C_3H_8 + CH_4$	3.85×10^{11}	65,250
$C_3H_8 \xrightleftharpoons{k_3} C_2H_2 + CH_4$	9.81×10^8	36,920
$C_2H_2 + C_2H_4 \xrightarrow{k_4} C_4H_6$	1.03×10^{12}	41,260
$C_2H_4 + C_2H_6 \xrightarrow{k_5} C_3H_6 + CH_4$	7.08×10^{13}	60,430

Material Balance

For the case of the free radical scheme for ethane cracking, there are 8 species in total. The mass balance equation is given by; [1]

$$\frac{dF_j}{dx} = \left(\sum_i a_{ij} r_i \right) \left(\frac{\pi d_{tm}^2}{4} \right) \quad (1)$$

$$r_i = k_i \prod_j C_j \quad (2)$$

$$k_i = A_i \exp \frac{-E_i}{RT} \quad (3)$$

$$C_i = \left(\frac{F_j}{F_T} \right) \left(\frac{P}{RT} \right) \quad (4)$$

$$F_T = F_{steam} + \sum_i F_j \quad (5)$$

For $i=1, 2, 3, \dots$ number of reactions, and $j=1, 2, 3, \dots$ total number of species (excluding steam).

Energy Balance

The energy balance equation was written in terms of the heat of formation for each molecular species. Free radicals, being of much smaller concentrations than molecular species, are ignored in the following differential equations; [1].

$$\frac{dT}{dx} = \frac{q(x)\pi d_{in} - \sum_j \left[\Delta H_{fj} \frac{dF_j}{dx} \right]}{\sum_j F_j C_{pj} + F_{steam} C_{p,steam}} \quad (6)$$

$$\Delta H_{f,j} = (\Delta H_{f,298}^\circ)_j + \int_{298}^T C_{pj} dT \quad (7)$$

For $j= 1, 2, 3, \dots$ total number of molecular species.

Momentum Balance

The momentum balance equation was formulated to accommodate the calculation of the additional pressure drop in the bends by using a friction factor, F_r ; [1].

$$\frac{dP}{dx} = \frac{\sum_j \frac{dF_j}{dx} + \frac{1}{M_m} \left(\frac{1}{T} \frac{dT}{dx} + F_r \right)}{\frac{1}{PM_m} - \frac{g_c P}{G_m^2 RT}} \quad (8)$$

The friction factor for straight tubes given by

$$F_r = 0.092 \frac{R e^{-0.2}}{d_{in}} \quad (9)$$

The friction factor for bends is given by

$$F_r = 0.092 \frac{R e^{-0.2}}{d_{in}} + \frac{\xi}{\pi R_b} \quad (10)$$

Where

$$\xi = \left(0.7 + 0.35 \frac{\Lambda}{90^\circ} \right) \left(0.051 + 0.19 \frac{d_{in}}{R_b} \right) \quad (11)$$

and

$$R_b = \frac{d_{in} G_m}{\mu_m} \quad (12)$$

The heat-flux profile in the radiation section of the reaction system was represented by a quadratic expression that is a function of a fraction of the total length of the reactor, L

$$q(x) = \alpha + \beta \left(\frac{x}{L} \right) + \gamma \left(\frac{x}{L} \right)^2 \quad (13)$$

Where, α , β and γ are suitable coefficients. Design and operating conditions of the industrial ethylene reactor taken from ref 5 are listed in Table 2. The coefficients in eq. 13 are $\alpha = 96$, $\beta = -85.91$, and $\gamma = 42.955$, all in kW/m^2 , which provide a heat-flux profile matching the per-tube heat-flux values given in ref. 1. Predictions of the reactor exit conditions by the model are

compared with the industrial data in Table 3; which shows that the model based on the free-radical mechanism is quite accurate.

Table: 2. Design and Operating Conditions for the Industrial Reactor [5]

Parameter	Value
inlet ethane-steam mixture temperature (K)	953
inlet ethane-steam mixture pressure (kPa)	303
steam-to-ethane mass ratio (SR)	0.4
inlet ethane flow rate ($kmol/s$)	0.020 87
tube inside diameter (m)	0.108
number of straight tubes (each 8.941 m long)	10
number of bends (each 0.559 m long)	10
total reactor length (m)	95

Results and Discussions

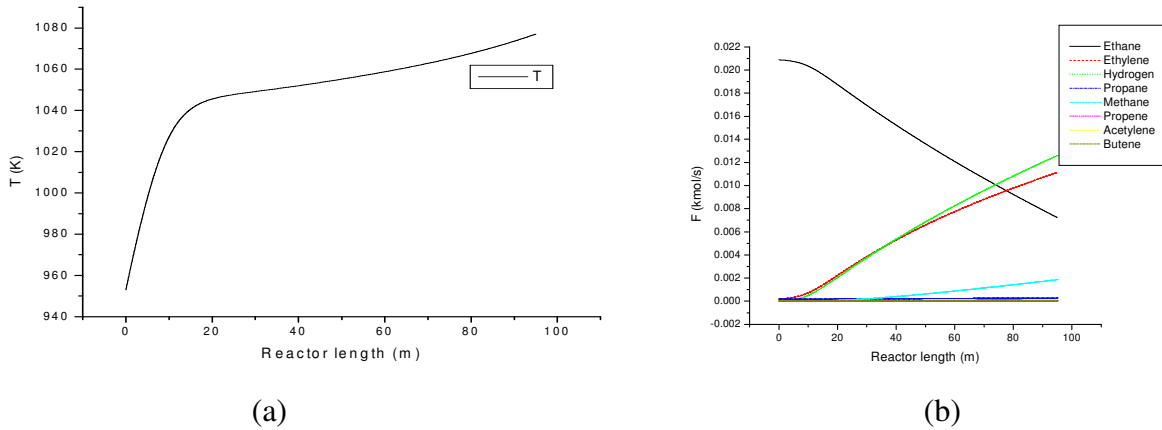


Fig. 1: Simulation results of ethane cracker

Figs. 1 (a-b) presents the simulation results of the ethylene cracker. From the Fig. 1 (a) it can be inferred that temperature increases rapidly in the initial length of the tube whereas in the later section temperature variation is less. Also it can be seen that pressure decreases gradually along the length of the tube. **Parameter Sensitivity Analysis**

Effect of feed temperature

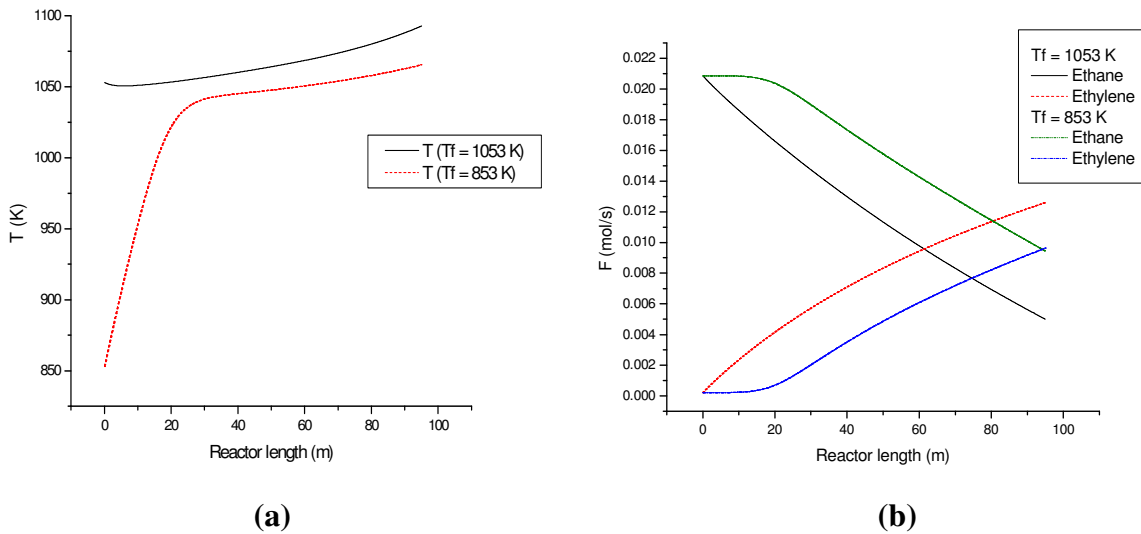
Fig. 2 compares the simulation results for the feed with temperature 853 K and 1053 K. It is observed that it gives a better conversion for the feed with temperature of 1053 K, the corresponding comparative simulation results have been shown in the Table 3.

Effect of internal diameter

A comparative simulation results (tubes with internal diameter 0.1143 m and 0.1080 m) has been shown in the Fig. 3 (a-b). Though the nature of the graphs are same for both the cases it is observed [from Table 4 and Figs. 3 (a-b)] that the tubes with internal diameter 0.1143 m gives better conversion as compared to the tubes with 0.1080 m internal diameter.

Table: 3. Comparison of Predictions by the Model with the Industrial Data

Parameter	Experimental values	Model prediction reported in [1] using model [4]	Model prediction (present study using Model 3 of [3])
coil outlet temperature (K)	1108	1121	1077.086
CH ₄ exit flow rate (kmol/s)	0.00131	0.0013	0.00186
C ₂ H ₄ exit flow rate (kmol/s)	0.0109	0.01109	0.01114
C ₂ H ₆ exit flow rate (kmol/s)	0.00822	0.007827	0.00723
C ₃ H ₆ exit flow rate (kmol/s)	0.000160	0.000137	.00007

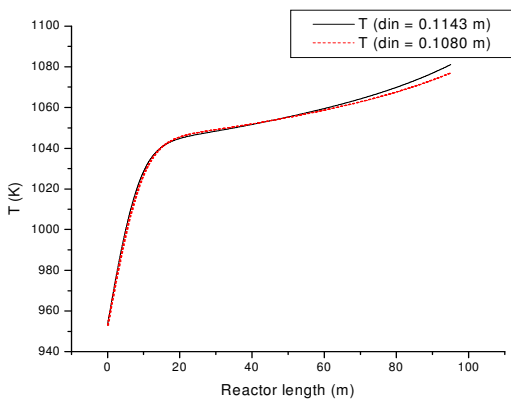
**Fig. 2: Sensitivity analysis – Effect of feed temperature**

Conclusions

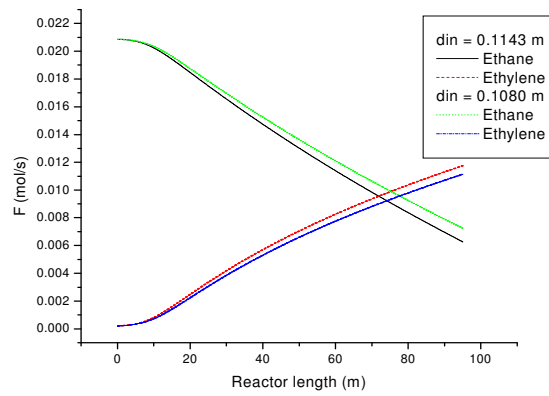
An industrial ethane cracker is simulated for the molecular reaction scheme with 8 components and 5 reactions (Model 3, Sundaram and Froment [3]). The simulated results have been compared with the industrial results and the results reported by Tarafder et al. [1] which includes the detailed reaction mechanism (with total 49 reactions having 11 molecular species and 9 free radicals) for ethane cracking (originally proposed by [4]). It is observed that the detailed model (as proposed by Sundaram and Froment [5]), gives accurate predictions. Also the effect of several process parameters is studied (using model proposed by Sundaram and Froment [3]) to investigate the performance of the ethane cracker for a change in the feed temperature and internal diameter of the tube.

Table: 3. Comparison of Predictions by the Model (Effect of temperature)

Parameter	Model prediction (T = 853 K)	Model prediction (T = 1053 K)	Model prediction (T = 953 K)
coil outlet temperature (K)	1065.519	1092.831	1077.086
conversion	0.833	0.902	.864
CH ₄ exit flow rate (kmol/s)	0.0014	0.00238	0.00186
C ₂ H ₄ exit flow rate (kmol/s)	0.00964	0.0126	0.01114
C ₂ H ₆ exit flow rate (kmol/s)	0.00943	0.005	0.00723
C ₃ H ₆ exit flow rate (kmol/s)	0.00007	0.00006	.00007



(a)



(b)

Fig. 3: Sensitivity analysis – Effect of internal diameter of the tube

Table: 4. Comparison of Predictions by the Model (Effect of internal diameter)

Parameter	Model prediction ($d_{in} = 0.1143$ m)	Model prediction ($d_{in} = 0.1080$ m)
coil outlet temperature (K)	1081.098	1077.086
CH ₄ exit flow rate (kmol/s)	0.00209	0.00186
C ₂ H ₄ exit flow rate (kmol/s)	0.01175	0.01114
C ₂ H ₆ exit flow rate (kmol/s)	0.00627	0.00723
C ₃ H ₆ exit flow rate (kmol/s)	0.00007	0.00007

Future Work

Model proposed by Sundaram and Froment [4] predicts accurate results in terms of temperature profile and concentration profile at the exit of the reactor. Model used in this study (Model 3, Sundaram and Froment [3]) does not provide accurate temperature and concentrations of the key components. Hence more focus can be given in future on the accurate modeling using the model originally proposed by Sundaram and Froment [4] to get exact profiles and subsequently to carry out optimization of ethane cracking process.

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