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Deterministic modeling of an industrial steam ethane cracker

Abstract

Rate-based deterministic modeling requires simple, yet sufficiently accurate modeling of complex petrochemical systems. In this work, steam ethane cracking was modeled with several molecular reactions, in addition to coke formation and coke removal by steam reforming reactions. A rate-based model was then developed which incorporates the reaction model together with momentum, energy and mass balances. The model consisted of nonlinear ODEs which were solved numerically. The developed model was then validated by the published experimental data from a pilot plant. Then it was utilized to simulate an industrial unit. This deterministic model simulates all the essentials of an industrial steam ethane cracking reactor so that optimum process parameters can be searched and determined.

Keywords: rate-based modeling, steam ethane cracking, ethylene manufacture

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Introduction

Nowadays, rate-based deterministic modeling plays an essential role in the design, simulation and optimization of chemical process units, such as reactors. True understanding of the chemical reactions coupled with appropriate transport phenomena can enable reliable simulation of petrochemical reactors. The key in this endeavor is the availability of accurate intrinsic reaction kinetics data. In recent years, significant progress has been achieved in predicting the behavior of industrially important complex petrochemical reaction systems such as steam cracking of paraffinic streams.[1–3] Commonly, the developed models are tested for laboratory-scale units. Accordingly, modeling and validation with real industrial units is still scarce. In this work, an industrial steam ethane cracker has been investigated as a test case for several reasons. First, it is a well-established petrochemical process and the detailed molecular and radical chemistry is fairly well known.[3–9] Second, reactor internals are relatively simple so that hydrodynamics can be formulated accurately. Indeed, in-house developed, reaction kinetics (CRACKSIM).[3,5,7,8] and reactor modeling tools (COILSIM)[10] for steam cracking have been published. There are also advanced furnace models which can predict increases in coke layer - hence increase in metal temperature. However, there is still a need for simple yet accurate models which can quickly predict furnace behavior. Such a model can then be extended to new furnace configurations, such as "split cracking" where a single mega furnace is used to crack both gas and liquid feedstocks.

Ethylene production

Ethylene is the most important and versatile building block intermediate of any olefinic petrochemical complex. It cannot be found naturally in hydrocarbon sources, such as natural gas and petroleum. Therefore, it has to be manufactured. Ethylene is mainly produced by steam cracking of paraffinic feedstocks such as ethane (gas-based) and light straight-run naphtha (liquid-based).[11] Depending on the prevailing conjuncture LPG, atmospheric gas oil (AGO), vacuum gas oil (VGO) –amongst others- can also be cracked. The source of ethane is mainly "associated gas" which is co-produced at oil and shale gas fields. Interestingly, while cracking LPG, naphtha, AGO, and VGO significant amount of ethane is also co-produced which is recovered and recycled as feed to a separate ethane cracker or a mega split cracker? Paraffinic feed stocks have both C-C and C-H bonds and their bond energies are 345 and 413kJ/mole respectively. Consequently, steam cracking is an endothermic process and by breaking the C-C bonds of big molecules -rather than C-H bonds-smaller molecules are produced. 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.[11] The furnace usually consists of convection and radiation sections where the feedstock first enters the convection section so that the hot flue gas preheats the feed before it enters the radiation section. Typical inlet temperatures to the radiant tube range from 500 to 600°C.[11] On the other hand, Millisecond Technology of KBR Co. employs furnaces with one type of coil-namely radiant at 700°C–which can also result in much lower residence times. In ordinary crackers, steam is introduced at an intermediate point in the convection section, and is preheated together with the feedstock. Typical steam requirements are as given in Table 1. Steam–which is an inert- lowers the partial pressure of hydrocarbons which is necessary from the point of reaction thermodynamics as the pyrolysis reactions increase the number of moles. In addition, steam lowers the partial pressure of high-molecular weight aromatics, reducing undesired condensation reactions. Finally, it contributes to the partial removal of coke in the tubes through steam reforming. The radiant coil is directly heated by the burners, leading the process gas to the cracking temperature, which ranges from 850 to 950°C. The temperature at the outlet of the radiant coil typically ranges from 775 to 885°C.[11] The reactor effluent is quickly quenched to prevent further reactions, compressed and sent to a separation unit of sequential distillation columns, for the recovery of ethylene and other products such as methane, ethane, propane, propylene, C4's and pyrolysis gasoline. Naturally, ethylene yield is much higher for gas-based crackers while naphtha produces more C4's and aromatic-rich pyrolysis gasoline.

Reaction mechanism modeling

The reaction mechanism of steam cracking of hydrocarbons to form ethylene can be formulated in different ways, namely, according to molecular and free-radical mechanisms, of which the last is the most detailed and perhaps the most accurate one.[12] Froment et al.[13,14] 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 problematic stiff differential equations that are difficult to solve.[15] For instance, Sundaram et al.,[16] developed a free-radical scheme for ethane cracking, where 49reactions were proposed and products heavier than C_5H_{10}, whose yields are usually very small, were lumped together as the single component C5+ 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.[17,18] Rangaiah et al.[19] evaluated several reaction schemes for ethane cracking, including the molecular[15] and the free-radical schemes[16] which were proposed by Froment and his group, and concluded that molecular mechanism is also acceptable.

Table 1 Steam requirements in steam cracking

Feed	***Kg steam /kg hydrocarbon***
Ethane	0.2-0.4
Propane	0.3-0.5
Naptha	0.4-0.8
Gas oil	0.8-1.00

Modeling the steam ethane cracker

In the present study, first the model developed by Froment et al.,[13] has been used as the basis for simulation. Here a molecular scheme with several reactions was adapted (Figure 1). The mass flow inside the reactor, which has a large length-to-diameter ratio and a high fluid velocity,[20] can be taken as plug flow. Nearly 90% of the heat transfer is accomplished by radiation mechanisms, namely between hot flue gases/coil and between refractory walls/coil. Since the reactions involved are extremely endothermic (1.6-2.8MJ/kg HC converted) very high heat fluxes, typically 75-85kW/m^2 coil, are needed thus uncoupling the reactions and thermal phenomena occurring inside the tubes from those occurring outside. A one dimensional axial model was used for the mass, momentum, and heat-transfer, as high turbulence in the reactor tubes would effectively cancel out gradients in radial direction[21] leading to the following equations:

Mass balance:

$$\frac{dF_j}{dz} = R_j * \frac{\pi d_t^2}{4} = \left(\sum_i \alpha_{ij} * r_i\right) * \frac{\pi d_t^2}{4} \qquad (1)$$

$$r_i = k_i \prod C_j^{\alpha_j} \qquad (2)$$

$$C_j = \frac{F_j}{\sum_{j=1}^{n} F_j} \frac{P_t}{RT} \qquad (3)$$

$$\sum_{j=1}^{9} F_j c_{pj} * \frac{dT}{dz} + \frac{\pi d_t^2}{4} \sum_i \Delta H_i * r_i = q(z) * \pi d_t \qquad (4)$$

Energy balance:

$$\frac{dT}{dz} = \frac{1}{\sum_{j=1}^{9} F_j c_{pj}} \left[q(z) * \pi d_t + \frac{\pi d_t^2}{4} \sum_i (-\Delta H_i) * r_i \right] \qquad (5)$$

Momentum balance:

$$-\frac{dP_t}{dz} = \left[\frac{2f}{d_t} + \frac{\zeta}{\pi r_b} \right] * \rho_g u^2 + \rho_g u \frac{du}{dz} \qquad (6)$$

These differential equations were then solved by using MATLAB© to obtain composition, temperature and pressure profiles along the reactor. Details of these calculations can be found elsewhere.[22] The important model parameters–amongst others- are:

i. composition and mass flow rate of charge,
ii. steam dilution ratio, and
iii. inlet and outlet temperatures of tube making the system an ideal multivariate optimization study case.[23]

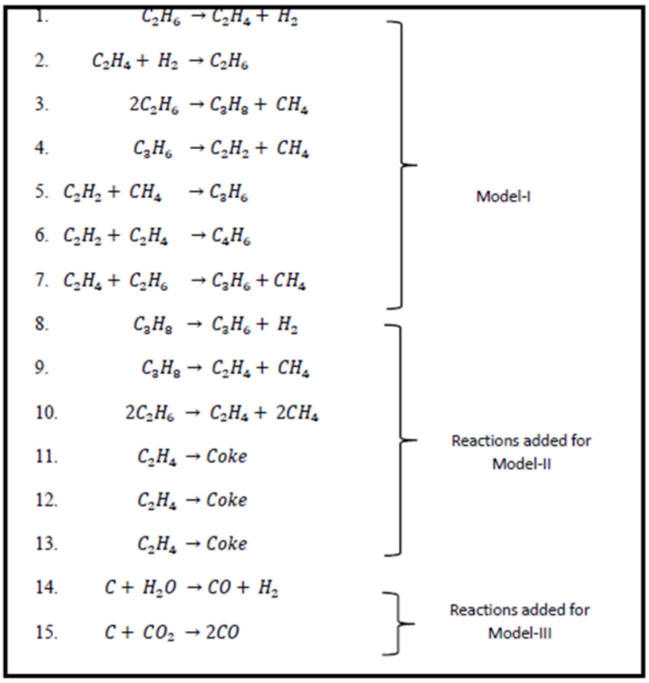

Figure 1 Simplified molecular schemes for Model I, II and III.

However, the ranges of temperatures depend also on molecular weight and exit temperature of 800-850°C is typical for ethane crackers. Since the reactions are endothermic, the wall temperature is well above these average temperatures which enhance coke formation at the tube wall resulting in increased fuel consumption in the furnace. The coke deposits on the walls of reactor reduce the overall heat transfer coefficient and increase the pressure drop along the reactor. This results in gradual decrease with run time of both the reactor tube metal temperature and the pressure drop across the reactor necessitating periodic shut down. Indeed, after a certain run length, the tubes have to be cleaned. Therefore, the reactor exit temperature and the radiant coil tube metal temperature are controlled carefully in order to prevent unnecessarily high temperatures.[23] The governing nonlinear differential equations were first solved without considering the coke formation and named as model I. Then, this model is modified to take into account some more reactions and coke formation equation which is directly related to temperature profile (Model II). Finally, simultaneous coke removal by steam reforming was considered (Model III) as shown in Figure 1. The rate expressions and the relevant reaction kinetics data for coke formation and for coke removal are given in Table 2.

Results and discussions

Model I is the simplest approach and does not take into account both coking and steam coke reforming. It is the same model as given by Froment et al.[15] Model II considers coke formation.[25,26] Finally,

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Model III considers not only coke formation but also coke removal due to simultaneous steam reforming whose reaction kinetics data are given in Table 2 & 3. It is a known fact that steam reforming requires a catalyst. It is presumed that Ni in stainless steel acts as a catalyst for coke formation.[27] and also for steam reforming of coke. Indeed, dimethyldisulfide (DMDS) is often used to eliminate or decrease the catalytic activity of Ni which is present in steel pipes. Figure 2 and Figure 3 compare simulation results of Model II with experimental data. Figure 4 compares the results of Mode III with Yanchesmesh's data (2) indicating reasonable agreement. Figure 3 shows the results of Model III which takes into account both coke formation and coke removal due to steam reforming in comparison with literature data.[28] After validation of Model III, this model was compared with the results of an industrial unit in Figure 5 for the temperature profile. It was therefore possible to see the coke and ethylene formations along the tube upon increasing the furnace duty. When the results in Figure 4 together with Figure 5 and Figure 6 are compared it is seen that when the temperature in the tubes increase both coke and ethylene formations increase. However, on the long term, coke deposition results in a fall in the thermal efficiency of furnace. Model can also give predictions for the metal temperature so that cracking of tubes can be predicted.

Table 2 Rate expressions added for Model-III[28]

Rate Expression	Reaction
$r_{12} = k_{12}\left[\frac{F_{H_2O}}{F_t}P_t\right]$	$C + H_2O \rightarrow CO + H_2$
$r_{13} = k_{13}\left[\left(\frac{F_{CO_2}}{F_t}P_t\right)^{0.31}\right]$	$C + CO_2 \rightarrow 2CO$

Table 3 Kinetic parameters added reaction for model-III

Rate Coefficient	A (s-1 or l mole-1s-1)	E (j/mole)
k_{12}	5.09xE4	2.38xE5
k_{13}	1.12xE8	2.45xE5

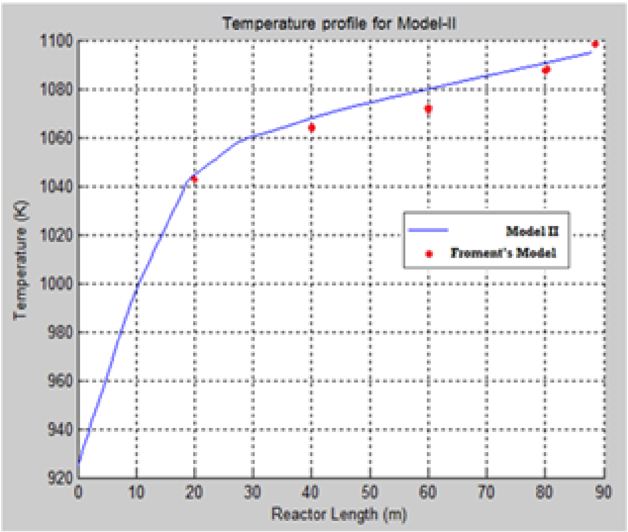

Figure 2 Temperature profile.

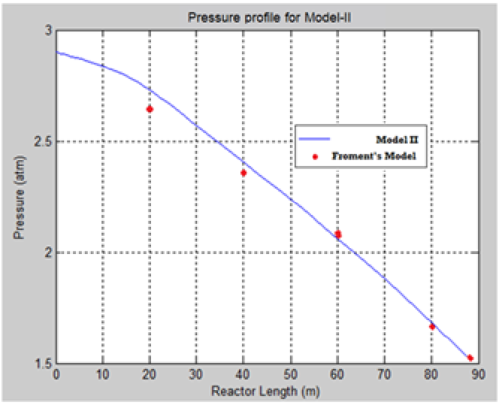

Figure 3 Pressure profile.

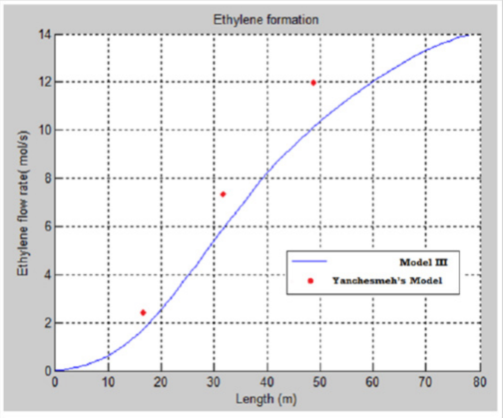

Figure 4 Ethylene profile in the tube.

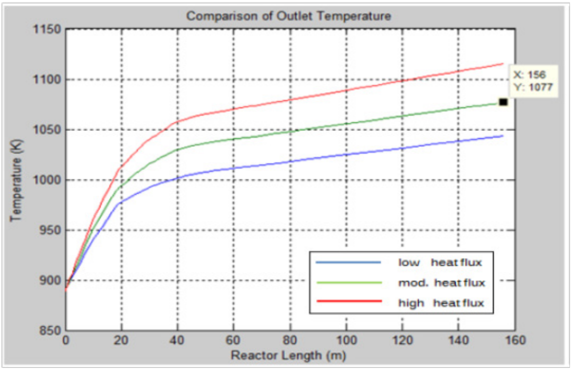

Figure 5 Temperature profiles at different furnace duties.

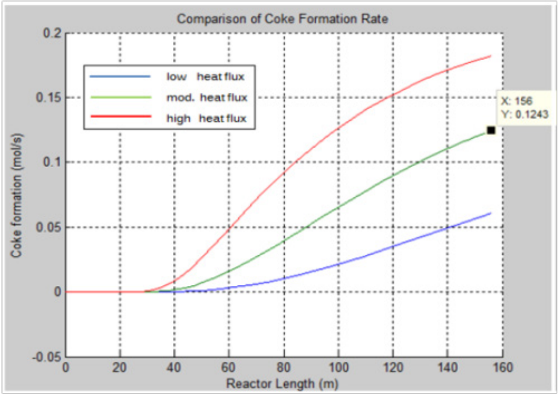

Figure 6 Coke formation at different furnace duties.

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Conclusion

Rate-based deterministic modeling can be a valuable simulation and optimization tool for petrochemical reactors. The key issue is to establish a reaction network model which is simple but is sufficiently representative of real complex system.[29] As an example, steam ethane cracking can be modeled and industrial crackers can be simulated. Such simulations may serve finding optimum conditions of process variables. For instance, Model III developed here consists of 8 molecular reactions in addition to coking formation and coke removal by steam reforming can estimate accurately essentials of an industrial steam cracking reactor, such as the temperature profile inside the tube. Therefore, effect of process variables can be investigated so that the unit is operated at optimum conditions (Table 4).

Table 4 Nomenclature

Symbol	Definition	Unit
C_j	Concentration of component j	kmol/m^3
c_pj	Specific heat capacity of component j	J mol/K
d_t	Diameter of the tube	m
F	The exchange factor	
f	Fanning friction factor	
F_j	Molar flow rate of component j	mol/s
Ft	Total molar flow rate of process gas	mol/s
G	Mass flux	kg/m^2.s
G_f	Flue gas mass flow rate	kg/h
H	Height of the furnace	m
L	Length of the furnace	m
L_{tube}	Total length of the tubes	m
M_m	Molecular weight of the gas	kg/kmol
P_c	Critical pressure	atm
P_t	Total Pressure	atm
Q(z)	Heat flux along the length z	j/m^2
Q_g	The enthalpy of flue gas	
Q_n	The net heat release	j/s
q_{rad}	The average radiant heat flux	jj/s/m^{2}s
Q_{total}	The total radiant heat amount	
R	Ideal Gas Constant	J/mo K
R_b	Radius of the bend	m
R_e	Reynolds Number	
R(i)	Rate of reaction i	kmol/m^3 s
T	Temperature	K
T_c	Critical temperature	K
T_t	Mean tube wall temperature	K
u	Velocity of the gas	m/s
V_c	Critical volume	m^3/kmol
z	Length	m
Z_c	Compressibility factor	
z_{ent}	The fraction of excess air	
x_{excess_air}	Excess air to burners	
ΔH_i	Heat of reaction of component i	j/mol
ΔH_f	Heat of formation of component j	j/mol
ϕ	Emissivity of the furnace	
η	Furnace Efficiency	%
α	The absorptivity of the tubes	
α_{ij}	Stoichiometric coefficient component j in reaction i	
ζ	Nekrasov factor	
μ	Viscosity of mixture	Pa s
ξ	Angle described by the bend	
ρ_g	Density of the gas	kg/m^3

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None.

Conflicts of interest

The author declares that there are no conflicts of interest.

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