MATHEMATICAL MODEL FOR THERMAL CRACKING OF HYDROCARBONS

ETHANE CRACKING

The simulation of a thermal cracking coil requires integration of a set of

- Mass balance
- Energy balance
- Momentum balance equations.

Mass Balance

$$\frac{dF_j}{dz} = - \Sigma(s_{ij} r_i) \frac{\pi d_t^2}{4} \qquad (1)$$

Reaction Mechanism for Ethane Cracking

$C_2H_6 \rightarrow CH_3^* + CH_3^*$

$CH_3^* + C_2H_6 \rightarrow CH_4 + C_2H_5^*$

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

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

$H^* + H^* \rightarrow H_2$

$H^* + CH_3^* \rightarrow CH_4$

$H^* + C_2H_5^* \rightarrow C_2H_6$

$C_2H_5^* + CH_3^* \rightarrow C_3H_8$

$C_2H_5^* + C_2H_5^* \rightarrow C_4H_{10}$

Reaction scheme for ethane cracker model

	E (kcal/kmol)	A
$C_2H_6 \leftrightarrow C_2H_4 + H_2$	72712	1.24E15
$C_2H_4 + 2H_2 \leftrightarrow 2CH_4$	58600	2.50E08
$C_2H_4 \rightarrow 0.125C_4H_8 + 0.125C_4H_{10} + 0.25\ C_4H_6 + 0.125H_2$		
$C_2H_4 \rightarrow 1/3\ C_6H_6 + H_2$	66800	1.80E09
$C_2H_4 \rightarrow C_2H_2 + H_2$	61600	4.00E08
$C_2H_4 \rightarrow 2C + 2H_2$	49000	5.81E05
$C_2H_4 + C_2H_6 \leftrightarrow 0.381C_3H_8 + 0.952C_3H_6 + 0.62H_2$	92400	0.94E14

Reaction rates

$r_1 = A_1 \exp(-E_1/RT) (pp(C_2H_6) - pp(C_2H_4)*pp(H_2)/Kp_1)$

$r_2 = A_2\exp(-E_2/RT)\ pp(C_2H_4) \sqrt{}pp(C_2H_6)pp(H_2) - pp(CH_4)/Kp_2)$

$r_3 = 0.012\ r_1\ P$

$r_4 = A_4 \exp(-E_4/RT)\ pp(C_2H_4)^2$

$r_5 = A_5 \exp(-E_5/RT)\ pp(C_2H_4)^2$

$r_6 = A_6 \exp(-E_6/RT)\ pp(C_2H_4)^2$

$r_7 = A_7 \exp(-E_7/RT) (pp(C_2H_4) - pp(C_2H_4)*pp(H_2)/Kp_1)$

Material balance equations

$d_{C2H6}/dZ = \Pi d^2/4 \quad (-r_1-r_7)$

$d_{CH4}/dZ = \Pi d^2/4 \quad (2\ r_2)$

$d_{C2H4}/dZ = \Pi d^2/4 \quad (r_1 - r_2 - r_3 - r_4 - r_5 - r_6 - r_7)$

$d_{C3H8}/dZ = \Pi d^2/4 \quad (0.381 r_7)$

$d_{C3H6}/dZ = \Pi d^2/4 \quad (0.952 r_7)$

$d_{C2H2}/dZ = \Pi d^2/4 \quad (r_5)$

$d_{H2}/dZ = \Pi d^2/4 \quad (r_1 - 2r_2 {}_{+\,0.125}\ r_3 + r_4 + r_5 + 2r_6 + 0.62 r_7)$

$d_{C4H10}/dZ = \Pi d^2/4 \quad (0.125 r_3)$

$d_{C4H8}/dZ = \Pi d^2/4 \quad (0.125 r_3)$

$d_{C4H6}/dZ = \Pi d^2/4 \quad (0.25 r_3)$

$d_{C6H6}/dZ = \Pi d^2/4 \quad (0.333 r_4)$

$d_{C}/dZ = \Pi d^2/4 \quad (2 r_6)$

Energy Balance

$$\frac{dT}{dz} = \frac{1}{\sum F_i Cp_i}\left[Q(z)\,\pi d_t + \frac{\pi d_t^2}{4}\, r_i\,(-\Delta H_i\,)\right]$$

Cp = specific heat

Q = heat flux

d_t = coil diameter

r_i = rate of reaction

ΔH = heat of reaction

- In order to avoid the complications of solving the above energy balance equation with the heat transfer coefficients, specific heats of each component, the heat flux profiles and heat of reaction, we have applied directly temperature profiles being used in industrial ethane cracker across the length of the reactor, in a polynomial form.

Momentum balance

- The pressure drop equation along the length of the cracking coil was derived by rapid estimates.

- In most empty tubular reactors kinetic energy changes are negligible and only the friction losses need be considered.

- The friction losses can be obtained from

$$f = \frac{\Delta P}{\rho_f \, z \, u^2/2 \, g_c}$$

- In the Reynolds number ranges of steam cracking flow rates the friction factor for smooth tubes can be calculated using

$$f = 0.184/N_{Re}^{0.2}$$

where $N_{Re} = DG/\mu_m$. Pressure drop was calculated by combining the above two Equations.

$$\Delta P = \frac{1.77 \times 10^{-7} G^{1.8} \mu_m^{0.2} z}{D^{1.2} \rho_f}$$

$$\mu_m = \frac{\sum y_i \mu_i \sqrt{M_i}}{\sum y_i \sqrt{M_i}}$$

The viscosity of individual component is calculated by

$$\mu_i = \frac{33.3\,(\sqrt{MT_c})\,[f(1.33T_r)]}{V_c^{0.66}}$$

$$f(1.33T_r) = 1.058\,T_r^{0.645} - \frac{0.261}{(1.9T_r)^{0.8\log(1.9Tr)}}$$

- The above set of continuity equations for each species along with energy and pressure drop equations are numerically integrated using fourth order Runge-Kutta method to obtain the axial profiles of conversion, temperature, and pressure.

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COKING MODEL

- Thermal cracking of hydrocarbons is always accompanied with the formation of coke which deposited on the walls of the coil.

- Coke may be formed either directly from the feed stock and/or from the products. Many components from the feed and products are capable of yielding coke which are called the coke precursors.

- The coke deposited in the coil and in the TLX hampers heat transfer and thereby requiring higher tube skin temperature.

- The coke deposition also reduces coil diameter which in turn leads to higher inlet pressures which are detrimental to ethylene yield.

- The temperature increase of the tube wall and pressure drop necessitate shutdown of the plant for decoking.

- Rate of coke deposition depends on several factors such as feed stock, operating conditions, pyrolysis coil design, its material of construction and pre treatments given to the inner walls of the coil.

Coking kinetics and rate of coke deposition along the length of the cracking coil as a function of time have to be incorporated in the main pyrolysis model to able to simulate run length.

- This helps in predicting the coke thickness inside the coil which in turn predicts the run length of cracking coil for a given set of operating parameters and a desired yield pattern.

- The present model considers ethane, and ethylene as potential coke precursors for run length simulation of ethane cracking.

Coking reaction scheme for ethane cracker model

	E, Kcal/gmol	A	Reaction order (n)
Ethane → coke	76.9	2.01E15	1
Ethylene → coke	49.61	1.83E10	1

The rate of coke formation can be expressed as

$$r_c = \sum_{i=1}^{m} r_{ci}$$

m is number of precursors

$$r_{ci} = A_i \exp(-E_i / RT_f)\, c_i^{\,ni}$$

where c_i is the concentration of the coke precursor which can be expressed in terms of partial pressure and temperature.

- The initial gas temperature profile was maintained constant for the complete run length.

- The concentrations of the precursors, C_i, are generated by main reaction model along the length of coil. The average of concentrations at the entrance and exit of each pass is taken as the concentration of that particular pass.

- The continuity equation for coking is integrated by incrementing time in stepwise.
- We have taken 24 h as step length.
- The thickness of the coke deposited, b_{ck}, is calculated using the following relation (Lichtenstein, 1964).

$$b_{ck} = \frac{d_i}{2}\left(1 - \exp\left(\frac{\alpha_{ck}\, r_c\, t_s}{2\rho_{ck}}\right)\right)$$

The pressure drop in coked tube is calculated using

$$\Delta P_{ck} = \Delta P (G_{ck}/G)^{1.8} (d/d_{ck})^{1.2} (\rho_{ck}/\rho)$$

where ΔP is clean tube pressure drop.

- The total increase in inlet pressure is calculated and checked with the limiting value. Once the increase in the inlet pressure exceeds the limiting value the calculations are stopped and the corresponding time is reported as run length.

Decoking is considered necessary when one of the following criteria is satisfied

1. Inlet pressure exceeding the limiting value

2. External tube skin temperature exceeding 1080°C

External tube skin temperature

- The external tube skin temperature is calculated by using the following relations (Rase, 1977).

$$T_w = T + \Delta T_f + \Delta T_{ck} + \Delta T_w$$

$$\Delta T_f = \frac{Q_0 d_o}{} \; ; \; \Delta T_{ck} = \frac{Q_0 d_o}{} \; ; \; \Delta T_w = \frac{Q_0\, d_o\, b_w}{}$$

$$h_i d_{ck} \qquad\qquad \lambda_{ck} \; \bar{d}_{ck} \qquad\qquad \lambda_w \; \bar{d}$$

- where T is fluid temperature and ΔT_f is temperature drop across the film, ΔT_{ck} is temperature drop across the coke and ΔT_w is temperature drop across the tube wall.
- $h_{i,}$ inside heat transfer coefficient is calculated using Dittus Boelter relation

$$h_i = 0.023 \; \frac{\lambda_f}{d_{ck}} \left(\frac{dck \; G}{\mu}\right)^{0.8} \left(\frac{C_p \; \mu}{\lambda_f}\right)^{0.4}$$

THE INPUT

- Molecular weights
- Critical properties
- Step size for calculations
- Temperature profile equations
- Coil geometry
- Kinetic parameters

- Feed rate (Flow rate of ethane per coil, t/h)
- Dilution ratio
- Crossover temperature
- Coil outlet temperature
- Coil inlet pressure

THE OUTPUT

∗ Concentration profile

∗ Temperature profile

∗ Pressure profile

∗ Product yields and Run length with varying feed stock quality and operating conditions

∗ External tube skin temperature

PROPANE CRACKING

Reactions

1. $C_3H_8 \rightarrow C_2H_4 + CH_4$
2. $C_3H_8 \leftrightarrow C_3H_6 + H_2$
3. $C_3H_8 \rightarrow 0.5C_4H_{10} + 0.5C_2H_6$
4. $C_3H_8 \rightarrow 0.5CH_4 + 0.5C_3H_6 + 0.5C_2H_6$
5. $C_2H_6 \rightarrow C_2H_4 + H_2$
6. $C_2H_6 \rightarrow CH_4 + 0.5C_2H_4$
7. $C_2H_6 \rightarrow 0.5CH_4 + 0.5C_3H_8$
8. $C_3H_6 \rightarrow 1.5C_2H_4$
9. $C_3H_6 + H_2 \rightarrow CH_4 + C_2H_4$
10. $C_3H_6 \rightarrow C_2H_2 + CH_4$
11. $C_2H_4 + H_2 \rightarrow C_2H_6$
12. $C_2H_4 \rightarrow C_2H_2 + H_2$
13. $C_2H_4 \rightarrow 0.667C_3H_6$
14. $2C_2H_2 + H_2 \rightarrow C_4H_6$
15. $C_3H_6 + C_2H_2 \rightarrow C_5s$

Reaction rates (kmol/m3 sec)	A(sec-1) or * (m3/kmol s)	E (kcal/kmol)
$r_1 = kp_1\, pp(C_3H_8)$	2.62E09	44000
$r_2 = kp_2\, pp(C_3H_8)$	2.00E09	44000
$r_3 = kp_3\, pp(C_3H_8)$	2.20E09	54000
$r_4 = kp_4\, pp(C_3H_8)$	1.10E09	48000
$r_5 = kp_5\, pp(C_2H_6)$	0.34E13	60000
$r_6 = kp_6\, pp(C_2H_6)$	3.90E12	67000
$r_7 = kp_7\, pp(C_2H_6)$	0.20E11	59000
$r_8 = kp_8\, pp(C_3H_6)$	0.99E10	44200
$r_9 = kp_9\, pp(C_3H_6)pp(H_2)$*	1.00E15	60000
$r_{10} = kp_{10}\, pp(C_3H_6)$	1.40E10	50000
$r_{11} = kp_{11}\, pp(C_2H_4)pp(H_2)$*	0.68E13	52000
$r_{12} = kp_{12}\, pp(C_2H_4)$	7.70E13	76000
$r_{13} = kp_{13}\, pp(C_2H_4)$	1.40E11	51000
$r_{14} = kp_{14}\, pp(C_2H_2)pp(H_2)$*	9.90E10	36000
$r_{15} = kp_{15}\, pp(C_2H_2)pp(C_3H_6)$*	9.00E14	51000

Material Balance

$d(CH_4)/dz = r_1 + 0.5r_4 + r_6 + 0.5r_7 + r_9 + r_{10}$

$d(C_2H_4)/dz = r_1 + r_5 + 0.5r_6 + 1.5r_8 + r_9 - r_{11} - r_{12} - r_{13}$

$d(C_2H_6)/dz = 0.5r_3 + 0.5r_4 - r_5 - r_6 - r_7 + r_{11}$

$d(C_3H_8)/dz = -r_1 - r_2 - r_3 - r_4 + 0.5r_7$

$d(C_3H_6)/dz = r_2 + 0.5r_4 - r_8 - r_9 - r_{10} + 0.667r_{13} - r_{15}$

$d(C_2H_2)/dz = r_{10} + r_{12} - 2r_{14} - r_{15}$

$d(H_2)/dz = r_2 + r_5 + r_{12} - r_9 - r_{11} - r_{14}$

$d(C_4H_{10})/dz = 0.5r_3$

$d(C_4H_6)/dz = r_{14}$

$d(C_5s)/dz = r_{15}$

REACTION SCHEME FOR LPG CRACKING

No.	Reaction	A	E, Kcal/gmol	Source
1.	$C_2H_6 \leftrightarrow C_2H_4 + H_2$	3.052E13	64.13	E
2.	$2C_2H_6 \rightarrow C_3H_8 + CH_4$	3.750E12	65.25	E
3.	$C_2H_4 + C_2H_6 \rightarrow C_3H_6 + CH_4$	6.083E13	60.43	E
4.	$C_3H_8 \rightarrow C_2H_4 + CH_4$	4.992E10	50.60	P
5.	$C_3H_8 \leftrightarrow C_3H_6 + H_2$	6.888E10	51.29	P
6.	$C_3H_8 + C_2H_4 \rightarrow C_2H_6 + C_3H_6$	7.036E13	59.06	P
7.	$C_3H_6 \leftrightarrow C_2H_2 + CH_4$	4.404E11	59.39	P
8.	$C_2H_6 \leftrightarrow C_2H_4 + H_2$	3.652E13	65.21	P
9.	$2C_3H_6 \rightarrow 3C_2H_4$	1.544E11	55.80	P
10.	$C_2H_2 + C_2H_4 \rightarrow C_4H_6$	0.160E12	41.26	P
11.	$C_3H_6 + C_2H_6 \rightarrow 1\text{-}C_4H_8 + CH_4$	2.500E14	60.01	P
12.	$2C_3H_6 \rightarrow 0.5C_6^+ + 3CH_4$	0.123E08	45.50	P

13. $n\text{-}C_4H_{10} \rightarrow C_3H_6 + CH_4$	1.000E13	59.64	NB
14. $n\text{-}C_4H_{10} \rightarrow 2C_2H_4 + H_2$	7.500E14	70.68	NB
15. $n\text{-}C_4H_{10} \rightarrow C_2H_4 + C_2H_6$	4.099E12	61.31	NB
16. $n\text{-}C_4H_{10} \leftrightarrow 1\text{-}C_4H_8 + H_2$	9.637E12	62.36	NB
17. $C_3H_6 + H_2 \rightarrow C_2H_4 + CH_4$	4.770E09	35.0	NB
18. $C_2H_2 + C_2H_4 \rightarrow C_4H_6$	0.0920E12	41.26	NB
19. $i\text{-}C_4H_{10} \leftrightarrow i\text{-}C_4H_8 + H_2$	9.046E11	54.40	IB
20. $i\text{-}C_4H_{10} \rightarrow C_3H_6 + CH_4$	5.000E11	54.43	IB
21. $i\text{-}C_4H_{10} + C_2H_4 \rightarrow 2\text{-}C_4H_8 + C_2H_6$	1.320E09	30.24	IB
22. $i\text{-}C_4H_{10} \rightarrow C_3H_4 + CH_4$	2.954E15	74.0	IB
23. $C_3H_4 \rightarrow C_6^{+}$	3.504E04	14.5	IB
24. $C_2H_2 + C_2H_4 \rightarrow C_4H_6$	0.0920E12	41.26	IB

THERMAL CRACKING OF ETHANE-PROPANE MIXTURES

Reaction Scheme for the Cracking of Mixtures of Ethane and Propane

- The combination of both ethane and propane cracking models enabled a molecular reaction scheme for the cracking of mixtures of both the components.