Chemical Reaction Engineering

Practical Session 4

30 November 2018

Pyrolysis of propane in Plug Flow Reactors

1. ***Uniform, constant external temperature***

The pyrolysis of propane is carried out in a Plug Flow Reactor, with an internal diameter of $D = 11\ cm$, thickness of 1 cm and equivalent length of $L = 70\ m$. The metal conductivity is $\lambda_w = 15\frac{kcal}{mhK}$. The inlet feed, made up of $2000\frac{kg}{h}$ of C_3H_8 and $1000\frac{kg}{h}$ of steam, is at $T_{in} = 600\ °C$ and $P = 3\ atm$.

As a first approximation, the primary reactions of pyrolysis are described through a simplified, first-order model:

$$C_3H_8 \rightarrow C_2H_4 + CH_4 \qquad r_1 = k_1 C_{C3H8} \quad k_1 = A_2 e^{-\frac{E_2}{RT}} \qquad A_1 = 2.2 \cdot 10^{12}\ s^{-1} \quad E_1/R = 29500\ K$$

$$C_3H_8 \rightarrow C_3H_6 + H_2 \qquad r_2 = k_2 C_{C3H8} \quad k_2 = A_2 e^{-\frac{E_2}{RT}} \qquad A_2 = 7.3 \cdot 10^{11}\ s^{-1} \quad E_2/R = 28700\ K$$

Both the reaction are endothermic: $\Delta H_1 = 18750\frac{kcal}{kmol}$ and $\Delta H_2 = 30840\frac{kcal}{kmol}$.
The tubular reactor is inside a furnace, which provides the required heat. As a first simplification, we can assume that the gases inside the furnace, surrounding the reactor, are at $T_{gas}^{f} = 1000\ °C$.

a. Evaluate propane conversion obtained at the reactor outlet.
b. Then, evaluate the reactor performance in terms of profiles of temperature, external temperature of tubes and concentrations of different species.
c. Finally, verify that the external temperature of tubes does not exceed $1100\ °C$ to avoid the tubes collapse.

The external heat transfer coefficient was estimated to be uniform and constant and equal to $h_e = 0.080\ \frac{kcal}{m^2 Ks}$. The internal heat transfer coefficient can be estimated using the Dittus-Boelter formula:

$$Nu = 0.023 Re^{0.8} Pr^{1/3}$$

For simplicity we assume that the following properties of the mixture are independent of composition and temperature: $Cp_{mix} = 0.8\frac{kcal}{kg\ K}$, $\mu_{mix} = 3.8 \cdot 10^{-5}\frac{kg}{m\ s}$, $\lambda_{mix} = 3.194 \cdot 10^{-5}\frac{kcal}{mKs}$. The pressure drop can be considered negligible.

2. ***Radiation from furnace walls and furnace gases (nonlinear equation solution)***

We want to refine the analysis carried out in Exercise 1, by considering also the heat exchange due to radiation. In particular, two additional heat fluxes have to be accounted for: the radiative heat flux from the furnace walls and the radiative heat flux from the furnace gases. The furnace walls have the same uniform temperature of furnace gases, i.e. $T_{walls}^{f} = 1100\ °C$. The two radiative fluxes are given by:

$$q_{walls} = F\sigma\varepsilon\left(T_{f,walls}^4 - T_e^4\right)$$

$$q_{gas} = \beta\left(T_{f,gas}^4 - T_e^4\right)$$

where $F\sigma\varepsilon = 4 \cdot 10^{-8}\ \frac{kcal}{m^2hK^4}$ and $\beta = 1 \cdot 10^{-8}\ \frac{kcal}{m^2hK^4}$ and T_e is the temperature along the external surface of the reactor.

Answer the same questions required in Exercise 1. In particular, for evaluation of the total heat exchanged, a nonlinear algebraic equation must be solved inside the ODE system describing the species and energy balances.

3. ***Radiation from furnace walls and furnace gases (DAE system)***
   Repeat Exercise 2 by solving the system of differential and algebraic equations as a DAE system.

4. ***Evaluation of pressure drop***
   Extend Exercise 3 by adding the equation describing the evolution of pressure along the reactor. The reactor is horizontal and the term corresponding to the kinetic energy in the pressure equation can be neglected. The friction factor can be evaluated using the Blasius equation:

$$f = \frac{0.079}{Re^{1/4}}$$

5. ***Coke formation along the reactor (fouling effect)***
   Repeat Exercise 4 by considering the possible formation of coke along the reactor. In particular, the thickness s_{coke} of the coke layer can be described through the following linear function along the reactor:

$$s_{coke}(z) = s_{coke}^{max}\frac{z}{L}$$

Where z is the reactor axial coordinate and $s_{coke}^{max} = 10\ mm$. The thermal conductivity of coke is uniform and equal to $\lambda_{coke} = 3\frac{kcal}{mhK}$.

6. ***Sensitivity analysis***
   Perform a sensitivity analysis with respect to the main parameter/operating conditions for model developed in Exercise 5:
   - overall inlet flow rate (range: $2000\ \div\ 4000\ kg/h$), keeping constant the propane/steam ratio;
   - reactor internal diameter (range: $10\ \div\ 12\ cm$), keeping the tube thickness unchanged;
   - temperature of furnace gases and walls ($1000\ \div\ 1200\ °C$)

Continuously Stirred Tank Reactor

7. ***Isothermal CSTR with parallel reactions***
   The two following parallel reactions (liquid phase) occur in an isothermal CSTR at $T = 80\ °C$:

$A \rightarrow B \qquad r_1 = k_1 C_A \qquad k_1 = A_2 e^{-\frac{E_2}{RT}} \qquad A_1 = 3 \cdot 10^{14}\ s^{-1} \quad E_1 = 20000 \frac{cal}{mol}$

$A \rightarrow B \qquad r_2 = k_2 C_A \qquad k_2 = A_2 e^{-\frac{E_2}{RT}} \qquad A_2 = 2 \cdot 10^{13}\ s^{-1} \quad E_2 = 18000 \frac{cal}{mol}$

The reactor is fed with pure A at concentration $C_A^0 = 55 \frac{kmol}{m3}$. The total residence time is $\tau = 1\ min$. Evaluate numerically the outlet concentrations of species A, B and C and compare them with the analytical solution.

8. ***Adiabatic CSTR with parallel reactions***

The same reactor described in Exercise 7 is now working in adiabatic conditions. In particular, the inlet temperature is $T_{in} = 20\ °C$. Evaluate numerically the outlet temperature and the concentrations of species A, B, and C. Additional data are required:

Species	$\boldsymbol{H_f^0 (T_0 = 20\ °C)}$ $[\boldsymbol{kcal/kmol}]$	$\boldsymbol{Cp}$ $[\boldsymbol{kcal/kmol/K}]$
A	6000	5
B	5802	6
C	5620	4

9. ***Adiabatic CSTR with parallel reactions (false transient method)***

Repeat the previous exercise by solving the NLS of equations using the *"false transient"* method.