Methanol synthesis: assessment of the performances of a multi-tubular reactor

Methanol synthesis is performed in a multi-tubular reactor externally cooled by boiling water at 38 bar.

The main reaction involved in the methanol synthesis is:

$$CO_2 + 3\ H_2 \leftrightarrow CH_3OH + H_2O \quad (1)$$

Moreover, the Reverse Water Gas Shift takes also place:

$$CO_2 + H_2 \leftrightarrow CO + H_2O \quad (2)$$

The reactor consists of 7500 tubes with a diameter of 38 mm and a length of 8 m. A specific mass flowrate of G = 8 kg m^{-2} s^{-1} is fed to each tube where catalytic pellets with cylindrical shapes are loaded (d_p = 6 mm - h_p = 3 mm). As a first approximation, the overall heat transfer coefficient is constant along the tubes and equal to 860 W m^{-2} K^{-1}.

Based on the reported data, by assuming negligible pressure drops:

a) write the mass and heat balance equations for the bed adopting a pseudo-homogeneous model
b) evaluate the hot-spot temperature and the methanol content in the outlet stream
c) compute the overall productivity of methanol in terms of ton/year

By removing the assumption of negligible pressure drops:

d) evaluate the pressure drop along the reactor
e) write the mass, heat and momentum balance equations for the bed adopting a pseudo-homogeneous model;
f) evaluate the hot-spot temperature and the methanol content in the outlet stream
g) compare the results obtained at point (b) and (f) and discuss whether the assumption of isobaric reactor is correct

Physical-chemical properties:

$$\rho_{cat} = 1.98\ \mathrm{g/cm^3} \qquad \Delta HR_1 = -49600\ \mathrm{J/mol}$$

$$\varepsilon = 0.4 \qquad \Delta HR_2 = 41000\ \mathrm{J/mol}$$

$$\langle Cp_{mix} \rangle = 4.081\ \mathrm{kJ/kg\ K} \qquad \mu = 23.6 \cdot 10^{-6}\ Pa\ s$$

Composition (mol/mol) and operating conditions:

CO	CO_2	H_2	CH_4	CH_3OH	H2O	N_2
0.054	0.1009	0.5698	0.2358	0.0042	0.0009	0.0344

Inlet temperature: 245°C

Inlet pressure: 65 bar

Kinetic equations:

$$r_{MeOH} = k_{MeOH} \frac{p_{CO_2} p_{H_2} \left(1 - \frac{1}{K_{eq,MeOH}} \left(\frac{p_{H_2O} p_{MeOH}}{p_{H_2}^3 p_{CO_2}}\right)\right)}{\left(1 + K_{ad,1} \frac{p_{H_2O}}{p_{H_2}} + K_{ad,2} \sqrt{p_{H_2}} + K_{ad,3} p_{H2O}\right)^3}$$

$$r_{RWGS} = k_{RWGS} \frac{p_{CO_2} \left(1 - \frac{1}{K_{eq,RWGS}} \left(\frac{p_{H_2O} p_{CO}}{p_{H_2} p_{CO_2}}\right)\right)}{\left(1 + K_{ad,1} \frac{p_{H_2O}}{p_{H_2}} + K_{ad,2} \sqrt{p_{H_2}} + K_{ad,3} p_{H2O}\right)}$$

$$\mathrm{r\ in\ [mol/(kg_{cat}\ s)], p\ in\ [bar]}$$

$$k_{MeOH} = 1.07 \exp\left(\frac{36696}{RT}\right)$$

$$k_{RWGS} = 1.22 \cdot 10^{10} \exp\left(\frac{-94756}{RT}\right)$$

$$K_{ad,1} = 3453.38$$

$$K_{ad,2} = 0.499 \exp\left(\frac{17197}{RT}\right)$$

$$K_{ad,3} = 6.62 \cdot 10^{-11} \exp\left(\frac{124119}{RT}\right)$$

$$R = 8.314 \frac{J}{mol\ K} \quad - \quad \mathrm{T\ in\ [K]}$$

K. M. Vanden Bussche et al., Journal of Catalysis ***161****, 1–10 (1996)*

The equilibrium constants are: (T in K):

- Methanol synthesis from CO_2: $K_{eq}(T) = 10^{\left(\frac{3066}{T} - 10.592\right)}$
- Reverse water gas shift: $K_{eq}(T) = 10^{\left(-\frac{2073}{T} + 2.029\right)}$

Pressure drops:

Ergun's equation:

$$\frac{\Delta P}{L} = 150 \frac{(1-\varepsilon)^2}{d_{eq}^2 \varepsilon^3} \mu \frac{G}{\rho} + 1.75 \frac{(1-\varepsilon)}{d_{eq} \varepsilon^3} \frac{G^2}{\rho}$$

where $d_{eq} = 6 \frac{V_p}{A_p}$

Antoine Equation:

A	B	C	
3.55959	643.748	-198.043	$\log_{10}(p^0) = A - \frac{B}{T+C}$ T in [K], p^0 in [bar]