

INDUSTRIAL ORGANIC CHEMISTRY – EXERCISE 2

Methanol synthesis: design of the multi-stage adiabatic reactor

Methanol synthesis is carried out in multi-stage adiabatic reactors with intermediate cooling in order to maintain a high reaction rate.

The main reaction involved in the methanol synthesis is:



Since CO_2 is fed to the reactor, the following reaction takes also place:



By assuming that the intermediate cooling is carried out by means of external heat exchangers, the temperature of the reacting mixture leaving the exchanger is equal to 240 °C. The maximum temperature in the catalytic bed has to be lower than 270 °C to avoid catalyst deactivation. The pressure drops along the reactors are negligible.

Based on the reported data:

- write the mass and heat balance equations for the generic adiabatic bed adopting a pseudo-homogeneous model;
- evaluate the volume of the reactor and the number of beds required to obtain a molar fraction of methanol in the outlet stream equal to 0.061

Input data:

1. Physycal-chemical properties

$$\begin{aligned} \rho_{\text{catalyst}} &= 1.98 \text{g}/(\text{cm}^3) \\ \varepsilon &= 0.4 \text{ (void fraction of the catalyst bed)} \end{aligned}$$

$$\langle C_{p_{\text{mix}}} \rangle = 4.081 \text{kJ/kg}$$

$$\Delta H_{R1} \approx -23460 \text{cal/mol}$$

$$\Delta H_{R2} \approx 9510 \text{cal/mol}$$

2. Operating conditions

Absolute pressure: 51 bar
Feeding temperature: 513 K

	Q (kmol/h)	y _i
CO	2008.6	13.39%
CO ₂	1495.0	9.97%
H ₂	9500.2	63.33%
CH ₄	1996.2	13.31%
CH ₃ OH	0.0	0.00%
H ₂ O	0.0	0.00%
tot	15000	100.00%

3. Kinetic equations

KINETIC EQUATION [mol/g _{cat} /min]	Reaction constants
$R_1 = \frac{f_{\text{CO}} f_{\text{H}_2}^2 - \frac{f_{\text{CH}_3\text{OH}}}{K_{\text{eq},1}}}{\left(C_1 + C_2 f_{\text{CO}} + C_3 f_{\text{CO}_2} + C_4 f_{\text{H}_2}\right)^2}$	$C_1 = \exp \left[3.49 + 4883 \left(\frac{1}{T} - \frac{1}{506} \right) \right]$ $C_2 = \exp \left[2.53 - 39060 \left(\frac{1}{T} - \frac{1}{506} \right) \right]$ $C_3 = \exp \left[3.70 + 15948 \left(\frac{1}{T} - \frac{1}{506} \right) \right]$ $C_4 = \exp \left[1.54 + 8229 \left(\frac{1}{T} - \frac{1}{506} \right) \right]$
$R_2 = \frac{f_{\text{CO}_2} f_{\text{H}_2} - \frac{f_{\text{CO}} f_{\text{H}_2\text{O}}}{K_{\text{eq},2}}}{C_5}$	$C_5 = \exp \left[5.18 + 938 \left(\frac{1}{T} - \frac{1}{506} \right) \right]$
<p>f = fugacity, atm</p> <p>(P.L. Villa, P. Forzatti, G. Buzzi-Ferraris, G. Garone, I. Pasquon, I&EC Process Design & Development 24 (1985) 12)</p>	

To evaluate the equilibrium constants, the ΔG° of reaction are reported:

$$\Delta G_1^0 = -22.858 + 0.05602 \cdot T \quad (\text{K}) \quad \text{kcal/mol}$$

$$\Delta G_2^0 = 9.418 - 0.00907 \cdot T \quad (\text{K}) \quad \text{kcal/mol}$$

The fugacity are evaluate accordingly to what reported in [Exercise 1](#)