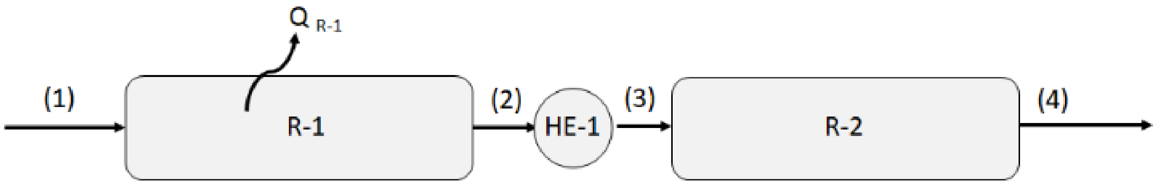
Methanol synthesis: analysis of the thermodynamic equilibrium

A simplified layout for the methanol synthesis consists of two reactors in series with intermediate cooling. The outlet stream from both reactors reaches thermodynamic equilibrium conditions and the following molecules are present: CO, CO_2, CH_3OH, H_2, H_2O, CH_4 (inert), N_2 (inert). The stream (2) leaving the first reactor is at 530 K. The heat exchanger between the reactors is designed to cool the stream to 480 K. The second reactor can be assumed as adiabatic. Pressure drop is negligible. The inlet stream is at 80 bar and 430 K.



By assuming a convenient model for the volumetric behavior and mixture, calculate:

1. The composition in stream (2)
2. The heat exchanged in reactor R-1 per unit of mole of stream (1)
3. The composition and temperature in stream (4)
4. The COx conversion across each reactor
5. The overall COx conversion

<u>Inlet compositions</u>:

Species	CO	CO_2	H_2	H_2O	CH_3OH	N_2	CH_4
Molar fraction [-]	0.054	0.1008	0.5696	0.0009	0.0042	0.0344	0.2361

Thermodynamic data:

Species	Tc [K]	Pc [bar]	ω [-]
CO	132.92	34.99	0.066
CO_2	304.19	73.82	0.228
H_2	33.18	13.13	-0.220
H_2O	647.13	220.55	0.345
CH_3OH	512.58	80.96	0.566
N_2	126.10	33.94	0.040
CH_4	190.58	46.04	0.011

Species	DH0F (298K) [cal/mol]	a	b x 10^3	c x 10^6	d x 10^9
CO	-26420	7.373	-3.07	6.662	-3.037
CO2	-94050	4.728	17.54	-13.38	4.097
H2	0	6.483	2.215	-3.298	1.826
H2O	-57800	7.701	0.4595	2.521	-0.859
CH3OH	-48080	5.062	16.94	6.179	-6.811
N2	0	7.44	-3.24	6.4	-2.79
CH4	-17890	4.598	12.45	2.86	-2.709

$C_{p,i}^{v}(T) = a_i + b_i \cdot T + c_i \cdot T^2 + d_i \cdot T^3$ [cal/mol/K] – gas phase

Methanol from CO: $\Delta G_R^0(T) = -22828 + 56.02 \cdot T$ [cal/mol] where T in [K]

RWGS: $\Delta G_{R,RWGS}^0(T) = 8514 - 7.71 \cdot T$ [cal/mol] where T in [K]

reference state: ideal gas at 1 atm

Peng & Robinson EoS

$$Z^3 + (B-1) \cdot Z^2 + (A - 3B^2 - 2B) \cdot Z + (B^2 + B^3 - AB) = 0$$

$$k = 0.37464 + 1.54226 \cdot \omega - 0.26992 \cdot \omega^2$$

$$a(T) = 0.45724 \cdot \frac{R^2 \cdot T_C^2}{P_C} \cdot \left(1 + k \cdot \left(1 - \sqrt{T_R}\right)\right)^2$$

$$b = 0.0778 \cdot \frac{R \cdot T_C}{P_C}$$

$$A = \frac{a(T) \cdot P}{(R \cdot T)^2}$$

$$B = \frac{b \cdot P}{R \cdot T}$$

$$\ln(\phi) = Z - 1 - \ln(Z - B) + \frac{A}{2\sqrt{2}B} \ln\left(\frac{Z + B\left(1 - \sqrt{2}\right)}{Z + B\left(1 + \sqrt{2}\right)}\right)$$

Solving procedure for the cubic equation

$$Z^3 + \alpha \cdot Z^2 + \beta \cdot Z + \gamma = 0$$
$$\alpha = B - 1$$
$$\beta = A - 3B^2 - 2B$$
$$\gamma = B^2 + B^3 - AB$$

$$p = \beta - \frac{\alpha^2}{3}$$
$$q = \frac{2\alpha^3}{27} - \frac{\alpha \cdot \beta}{3} + \gamma$$
$$D = \frac{q^2}{4} + \frac{p^3}{27}$$

If D>0, only 1 real solution is found.

$$Z = \left(-\frac{q}{2} + \sqrt{D}\right)^{\frac{1}{3}} + \left(-\frac{q}{2} - \sqrt{D}\right)^{\frac{1}{3}} - \frac{\alpha}{3}$$

If D = 0, 3 real solutions are found, of which 2 are identical.

$$Z_1 = -2 \cdot \left(-\frac{q}{2}\right)^{\frac{1}{3}} - \frac{\alpha}{3}$$

$$Z_2 = Z_3 = \left(-\frac{q}{2}\right)^{\frac{1}{3}} - \frac{\alpha}{3}$$

If D< 0, 3 distinct real solutions are found.

$$Z_1 = 2 \cdot r^{\frac{1}{3}} cos\left(\frac{\theta}{3}\right) - \frac{\alpha}{3}$$

$$Z_2 = 2 \cdot r^{\frac{1}{3}} cos\left(\frac{2\pi + \theta}{3}\right) - \frac{\alpha}{3}$$

$$Z_3 = 2 \cdot r^{\frac{1}{3}} cos\left(\frac{4\pi + \theta}{3}\right) - \frac{\alpha}{3}$$

$$r = \sqrt{-\frac{p^3}{27}}$$

$$cos(\theta) = -\frac{q}{2r}$$