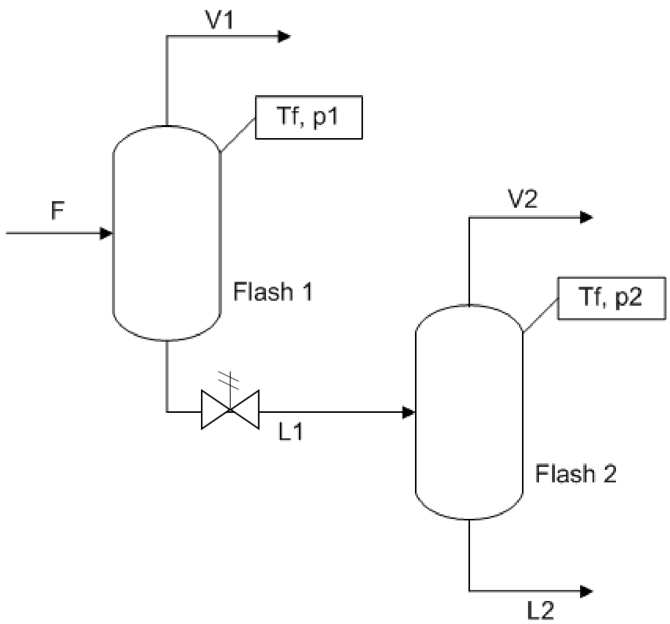
Methanol synthesis: design of the methanol separation units



The effluent stream from the reactor (F) is sequentially treated to separate the methanol from the unreacted species. The system consists of two sequential flash units. The first operates at the same pressure of the reactor (65 bar) and at 40 °C. The gas stream (V1) is recycled to the reactor after purge, while the liquid stream (L1) is laminated and sent to a second flash drum. The second flash operates at much lower pressure (5 bar) and at 40°C. The gas stream leaving is sent to the fuel gas line while the liquid stream goes to the distillation trains. Both flash units are isothermal.

It is required to evaluate:

1. The dew temperature of the F stream by considering the following hypothesis on the volumetric behavior of the gas and mixtures:
   a. Ideal gas and ideal mixture
   b. Real gas and real mixture
2. Evaluate the extent of vaporization of the first flash by assuming as volumetric behavior real gas and real mixture
3. Evaluate the flow rates and the composition of the streams (L1, V1) leaving Flash 1
4. By assuming as volumetric behavior of the flash ideal gas and ideal mixture, evaluate the extent of vaporization of Flash 2.
5. Evaluate the composition of the streams L2 and V2
6. Evaluate the duty to the Flash 2 by neglecting the contribution of the gas dissolved in the liquid streams for the case of Tf = 40°C

Operating conditions:

Absolute pressure Flash 1: 65 bar

Absolute pressure Flash 2: 5 bar

Flash temperature: 40 °C

Total inlet flow rate: 5330 kmol/h

Molar composition in stream F:

CO	0.036
CO_2	0.088
H_2	0.51
H_2O	0.023
CH_3OH	0.049
N_2	0.038
CH_4	0.256

Thermodynamic properties:

	Tc [K]	Pc [bar]	ω [-]	Cp_i^L [J/mol/K]	Cp_i^V [J/mol/K]	$\Delta h_i^{vap} @T_{boil,n}$ [kJ/mol]
CO	132.92	34.99	0.066	-	29.08	-
CO_2	304.19	73.82	0.228	-	38.40	-
H_2	33.18	13.13	-0.22	-	28.76	-
H_2O	647.13	220.55	0.345	75.55	34.58	39.50
CH_3OH	512.58	80.96	0.566	79.93	47.61	35.14
N_2	126.1	33.94	0.04	-	29.07	-
CH_4	190.58	46.04	0.011	-	36.33	-

The enthalpies of vaporization are given at the normal boiling temperature of the species.

Henry constant (H):

	CO	CO2	H2	CH4	N2
H(bar) @ T_f	2500	164	6200	1130	3660

Antoine equation:

	A	B	C
CH_3OH	5.2041	1581.34	-33.50
H_2O	6.2096	2354.731	7.559

$$\log_{10} p^0(T) = A - \frac{B}{C+T}$$

$T\ [K]$ - $p^0(T)$ [bar]

Equation of state (RKS):

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

Parameters:

$$a = \frac{0.42748 \cdot \alpha \cdot \left(R_{gas} \cdot T_C\right)^2}{P_C}$$
$$b = \frac{0.08664 \cdot R_{gas} \cdot T_C}{P_C}$$
$$\alpha = \left(1 + S \cdot \left(1 - \sqrt{T_R}\right)\right)^2$$
$$S = 0.48 + 1.574 \cdot \omega - 0.176 \cdot \omega^2$$
$$A = \frac{a \cdot P}{\left(R_{gas} \cdot T\right)^2}$$
$$B = \frac{b \cdot P}{R_{gas} \cdot T}$$

Parameters and mixing rules:

$$A_i = \frac{a_i \cdot P}{\left(R_{gas} \cdot T\right)^2}$$
$$B_i = \frac{b_i \cdot P}{R_{gas} \cdot T}$$
$$a_{mix} = \left(\sum_{i}^{NC} x_i \cdot \sqrt{a_i}\right)^2$$
$$b_{mix} = \sum_{i}^{NC} x_i \cdot b_i$$
$$A_{mix} = \frac{a_{mix} \cdot P}{\left(R_{gas} \cdot T\right)^2}$$
$$B_{mix} = \frac{b_{mix} \cdot P}{R_{gas} \cdot T}$$

Fugacity coefficients of specie *i* in mixture with composition x_i

$$\ln \hat{\phi}(T, P, \boldsymbol{x_i}) = \frac{B_i}{B_{mix}} \cdot (Z - 1) + \frac{A_{mix}}{B_{mix}} \cdot \left(\frac{B_i}{B_{mix}} - 2 \cdot \sqrt{\frac{A_i}{A_{mix}}}\right) \cdot ln\left(\frac{Z + B_{mix}}{Z}\right) - ln(Z - B_{mix})$$

Solving procedure for the cubic equation

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

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

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.

$$Z_1 = 2 \cdot r^{\frac{1}{3}} cos\left(\frac{\theta}{3}\right) - \frac{\alpha}{3}$$
$$Z_2 = 2 \cdot r^{\frac{1}{3}} cos\left(\frac{2\pi + \theta}{3}\right) - \frac{\alpha}{3}$$
$$Z_3 = 2 \cdot r^{\frac{1}{3}} cos\left(\frac{4\pi + \theta}{3}\right) - \frac{\alpha}{3}$$

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

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