## Exercise 2

CH3OH is used as a source to generate hydrogen for a vehicle fuel cell. Methanol and steam are introduced into a reforming plant. This plant converts these two streams into CO2, CO and H2, having also H2O in the outlet stream of the reformer.

Considering that the reactor is fed with 1 kg of CH3OH and 1 kg of H2O, the exit temperature of the products being 300ºC.
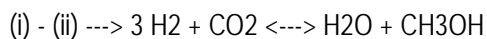   a) Determine the molar composition of the products for a pressure of 4 MPa and 5 MPa.
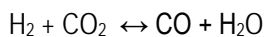   b)

The chemical reaction of reforming for steam:

$CH_3OH + H_2O \leftrightarrow 3\ H_2 + CO_2$

    CO + 2 H2 <---> CH3OH   (i)
    CO + H2O <---> H2 + CO2   (ii)
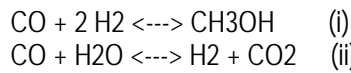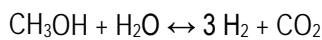
Subtracting both expressions:

    (i) - (ii) ---> 3 H2 + CO2 <---> H2O + CH3OH

$K_{SR} = (K_i/K_{ii})^{-1}$ for the reaction CH3OH + H2O <-----> 3 H2 + CO2

Where, in the reformer, the water gas shift reaction is:

$H_2 + CO_2 \leftrightarrow CO + H_2O$

The equilibrium constant is given as a function of the mole fractions or numbers of moles of the substances involved, depending on the temperature in degrees Kelvin.

$$K_{ii} = K_{WGS} = \frac{y_{CO}\,y_{H2O}}{y_{H2}\,y_{CO2}} = \frac{n_{CO}n_{H2O}}{n_{H2}n_{CO2}} = 1/\exp(-3.798 + 4160/T) \tag{1}$$

Fort he reaction: CO + 2 H2 <---> CH3OH (i)

According to the authors, Thomas & Portalski:

   $K_i = \exp(10.20 + 3921/T - 7.971 \cdot \log10(T) + 0.002499 \cdot T - 0.0000002953 \cdot T^2)$

According to the author, Kotowski:

   $K_i = \exp(8.729 + 3981/T - 7.411 \cdot \log10(T) + 0.002403 \cdot T + 0.000000215 \cdot T^2)$

The equilibrium constant is given as a function of the mole fractions or numbers of moles of the substances involved, depending on the temperature in degrees Kelvin.

$$K_{SR} = \frac{y_{H2}^3\, y_{CO2}}{y_{CH3OH}\, y_{H2O}} P_{TOT}^2 = \frac{n_{H2}^3\, n_{CO2}}{n_{CH3OH}\, n_{H2O}\, n_{TOT}^2} P_{TOT}^2 \tag{2}$$

The products obtained are: methanol (CH_3OH), carbon monoxide (CO), water (H_2O), carbon dioxide (CO_2), and hydrogen (H_2).

Assuming that 1 kmol of CH_3OH and α kmol of H_2O enter:

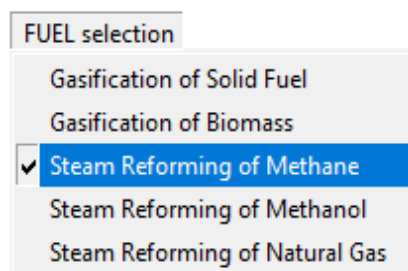| Chemical	Initial (mol)	Change (mol)	End (mol)
CH_3OH	1	$-x_1$	$1-x_1$
H_2O	α	$-x_1+x_2$	$α-x_1+x_2$
CO_2	0	x_1-x_2	x_1-x_2
CO	0	x_2	x_2
H_2	0	$3x_1-x_2$	$3x_1-x_2$
Moles totales	$1+α$	$2x_1$	$1+α+2x_1$

For a pressure other than 1 atm:

$$K_{SR} = \frac{(3x_1 - x_2)^3(x_1 - x_2)}{(1 - x_1)(α - x_1 + x_2)(1 + α + 2x_1)^2} P_{TOT}^2 = 10^{(2073/T - 2.029)} \tag{3a}$$

$$K_{WGS} = \frac{(x_2)(α - x_1 + x_2)}{(3x_1 - x_2)(x_1 - x_2)} = 1/\exp(-3.798 + 4160/T) \tag{3b}$$

Knowing the amount of kilograms that enter the methane and water reactor, it is very easy to obtain the value of moles of water (α) that enter.

α = kg H_2O/ kg CH_3OH (32/18) kmoles H_2O / kmoles CH_3OH = 1.777 kmoles H_2O / kmoles CH_3OH

The "THERMOGasification" software has the calculation algorithms explained in the previous problem. Using it, the following results are achieved:

ThermoGasification

ThermoSuite
Technical Software Suite

FUEL FEED
25	°C
100	kPa
	kg/s ☐

Hydrocarbon gas feed **Steam**

STEAM
	°C
	kPa
	kg/s ☐

Feed steam to fuel ratio
1,0000 ⬍ kg/kg

flue gas

STEAM REFORMING PLANT

Synthetic gas

PRODUCTS
300	°C ☑
Stack Temperature	
5000	kPa
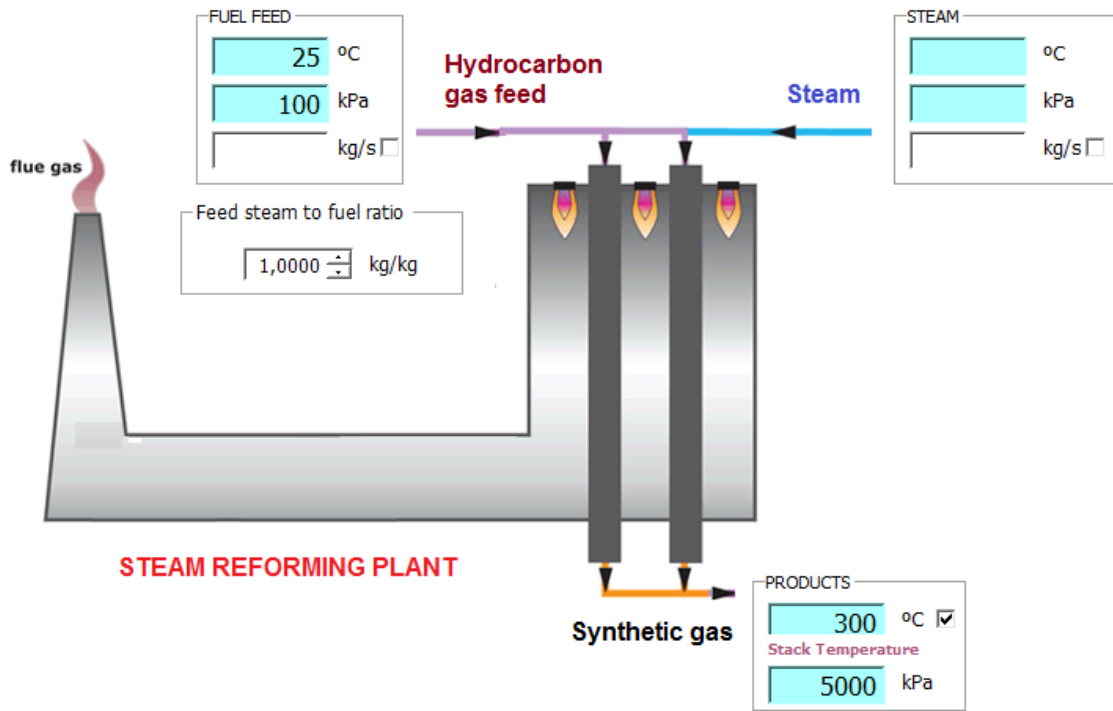
Equilibrium equations: ⓘ

Steam reforming reaction

$$CH_3OH + H_2O <---> 3\ H_2 + CO_2$$

Water gas shift reaction

$$CO_2 + H_2 <---> CO + H_2O$$

	Equilibrium constant	Dissociation	Relative error
	66299.7	0.962991	0
	0.0314255	0.086	0

Combustion Products FLUE GAS

☑ On wet basis ☐ On dry basis

	☐ mol/mol fuel	kg/kg fuel	Mole %	Mass %
CO_2	0.87699	1.20455	18.6411	60.2275
CO	0.08600	0.07518	1.8280	3.7590
H_2O	0.90162	0.50692	19.1646	25.3460
H_2	2.80297	0.17635	59.5793	8.8175
CH_3OH	0.03701	0.03701	0.7867	1.8505
TOTAL	4.7046	2.0000	100.00 %	100.00 %

PRODUCTS

300	°C	✓

Stack Temperature

4000	kPa

Equilibrium equations: ⓘ

	Equilibrium constant	Dissociation	Relative error
Steam reforming reaction $CH_3OH + H_2O <--->3\ H_2 + CO_2$	66299.7	0.975991	0
Water gas shift reaction $CO_2 + H_2 <---> CO + H_2O$	0.0314255	0.089	0

Combustion Products FLUE GAS

☑ On wet basis ☐ On dry basis

	mol/mol fuel	kg/kg fuel	Mole %	Mass %
CO_2	0.88699	1.21828	18.7501	60.9140
CO	0.08900	0.07780	1.8814	3.8900
H_2O	0.89162	0.50130	18.8479	25.0650
H_2	2.83897	0.17861	60.0129	8.9305
CH_3OH	0.02401	0.02401	0.5075	1.2005
TOTAL	4.7306	2.0000	100.00 %	100.00 %

Increasing the pressure decreases the production of hydrogen and CO_2. At a pressure of 4 MPa the ratio of H_2 produced to CO_2 produced is 3.200, while at a higher pressure of 5 MPa it is slightly lower than 3.196.