

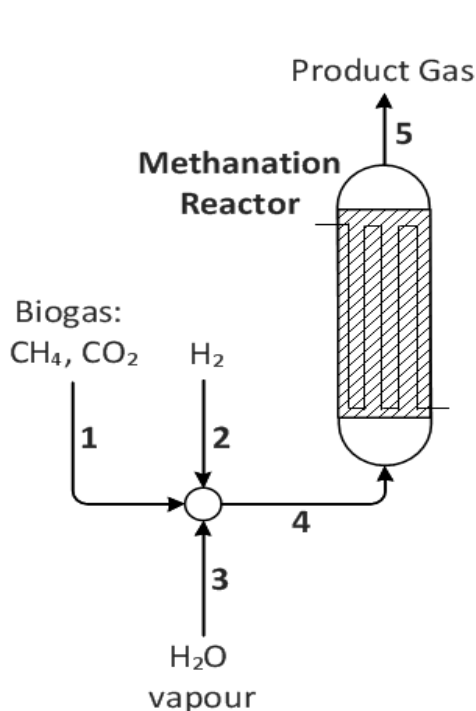
## Exercise 12: Methanation

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A detailed solution is provided at the **13<sup>th</sup> of December**.

Please see: <http://www.psi.ch/ene/ret1>

### Problem: Direct Methanation of Carbon Dioxide from Biogas

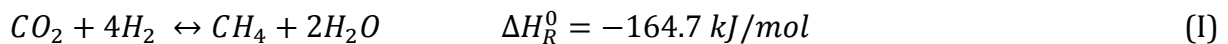


Biogas is produced via fermentation of biomass, e.g. green waste, sewage sludge or manure. After the fermentation a gas was built, which contains methane and carbon dioxide. Further upgrade is needed to reach gas grid quality with a minimum of 96% of methane. Conventionally carbon dioxide is separated via scrubbing and then released into atmosphere. In a new approach carbon dioxide is not seen as waste, but as raw material for further methane production. Here the raw biogas is entering a methanation unit, in which carbon dioxide and added hydrogen is converted to further methane. The already existing methane in the biogas is passing the methanation as quasi-inert. This procedure allows an increase of the bio-methane production up to 80% with the same amount of biomass at the input.

The direct methanation is illustrated in Figure 1. Here biogas (1) is mixed with hydrogen (2) and possibly with steam (3). The steam inhibits the deactivation of the catalyst due to carbon deposition. The mixture (4) enters the methanation reactor, where carbon dioxide and hydrogen convert to methane and water:

**Figure 1: Flowsheet of a direct methanation**

deactivation of the catalyst due to carbon deposition. The mixture (4) enters the methanation reactor, where carbon dioxide and hydrogen convert to methane and water:



The reactor is cooled by an internal heat exchanger. The outlet stream of the reactor (5) contains mainly methane and water.

### Tasks:

- i. **Methanation without steam:** Calculate the molar flows of all components in stream 5  $\dot{n}_{5,i}$  [mol/s] and the heat stream  $\dot{Q}_{out,M}$  [kW], which must be dissipated in order to maintain a temperature of  $T_{meth} = 320^\circ\text{C}$ . A steady state process is

assumed. Stream 4 has a temperature of  $T_4 = 270^\circ\text{C}$ . The conversion of  $\text{CO}_2$  in the methanation unit reaches  $C_{\text{CO}_2} = 95\%$ .

Further values:

- Biogas stream:  $\dot{n}_1 = 4 \frac{\text{mol}}{\text{s}}$ ,  $x_{1,\text{CH}_4} = 0.55$ ,  $x_{1,\text{CO}_2} = 0.45$
- In this case: No steam is added,  $\dot{n}_3 = 0 \frac{\text{mol}}{\text{s}}$ ,
- The ratio of  $\text{H}_2$  to  $\text{CO}_2$  in stream 4 is stoichiometric
- $p = 5 \text{ bar}$
- Specific heat capacities:  $c_{p,4\text{mix}} = 31.7 \frac{\text{J}}{\text{mol K}}$ ,  $c_{p,5\text{mix}} = 34.4 \frac{\text{J}}{\text{mol K}}$

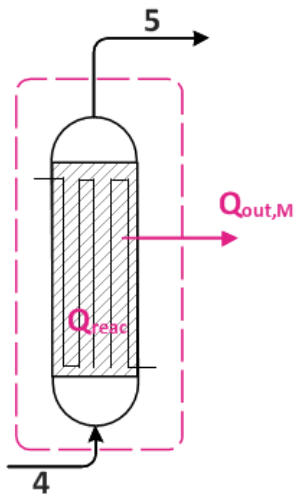
1. Determine the mole flows of  $\dot{n}_4$  :

$$\begin{aligned} \dot{n}_1 &= 4.0 \text{ mol/s} \rightarrow \dot{n}_{1,\text{CH}_4} = x_{1,\text{CH}_4} \cdot \dot{n}_1 = 2.2 \text{ mol/s} ; \dot{n}_{1,\text{CO}_2} = x_{1,\text{CO}_2} \cdot \dot{n}_1 = 1.8 \text{ mol/s} \\ \dot{n}_2 &= 4 \cdot \dot{n}_{1,\text{CO}_2} = 7.2 \text{ mol/s} \\ \rightarrow \dot{n}_{4,\text{H}_2} &= 7.2 \text{ mol/s} ; \dot{n}_{4,\text{CH}_4} = 2.2 \text{ mol/s} ; \dot{n}_{4,\text{CO}_2} = 1.8 \text{ mol/s} ; \dot{n}_{4,\text{H}_2\text{O}} = 0 \text{ mol/s} \end{aligned}$$

2. Determine the mole flows of  $\dot{n}_5$  :

$$\begin{aligned} \dot{n}_{5,\text{CO}_2} &= \dot{n}_{4,\text{CO}_2} \cdot (1 - C_{\text{CO}_2}) = 0.09 \text{ mol/s} \\ \dot{n}_{5,\text{CH}_4} &= \dot{n}_{4,\text{CH}_4} + \dot{n}_{4,\text{CO}_2} \cdot C_{\text{CO}_2} = 3.91 \text{ mol/s} \\ \dot{n}_{5,\text{H}_2} &= 4 \cdot \dot{n}_{4,\text{CO}_2} \cdot (1 - C_{\text{CO}_2}) = 0.36 \text{ mol/s} \\ \dot{n}_{5,\text{H}_2\text{O}} &= 2 \cdot \dot{n}_{4,\text{CO}_2} \cdot C_{\text{CO}_2} = 3.42 \text{ mol/s} \end{aligned}$$

3. Determine the heat stream, which must be dissipated to reach  $T_5 = 320^\circ\text{C}$  in the reactor:



$$\begin{aligned} \dot{Q}_{out,M} &= \dot{H}_5 - \dot{H}_4 + \dot{Q}_{reac} \\ \dot{H}_5 &= \dot{n}_5 \cdot c_{p,5\text{mix}} \cdot T_5 = 158.7 \text{ kW} \\ \dot{H}_4 &= \dot{n}_4 \cdot c_{p,4\text{mix}} \cdot T_4 = 192.8 \text{ kW} \end{aligned}$$

(Annotation:  $\dot{H}_5 < \dot{H}_4$ , although  $T_5 > T_4$  because of the mole decreasing reaction:  $\dot{n}_5 < \dot{n}_4$ )

$$\begin{aligned} \dot{Q}_{reac} &= C_{\text{CO}_2} \cdot \dot{n}_{4,\text{CO}_2} \cdot \Delta H_R^0 = -281.6 \text{ kW} \\ \rightarrow \dot{Q}_{out,M} &= 158.7 \text{ kW} - 192.8 \text{ kW} - 281.6 \text{ kW} = \\ &= -315.7 \text{ kW} \end{aligned}$$

Thus a heat stream of 326.8 kW must be dissipated in order to reach a reactor temperature of  $320^\circ\text{C}$ .

## ii. Equilibrium Constant

Calculate the equilibrium constant  $K_{\text{eq}}$  with thermodynamic data and check if the reaction reaches its equilibrium state. Use the NIST database in the appendix for standard enthalpy and entropy calculations at  $T_{\text{meth}}$ .

1. Calculate Standard Enthalpy of formation and Entropy for each component.

Correlation used by NIST database:

$$\Delta H_f^0(T) = A \cdot t + B \cdot t^2/2 + C \cdot t^3/3 + D \cdot t^4/4 - E/t + F - H + \Delta H_f^0(T^0)$$

$$\Delta S^0(T) = A \cdot \ln(t) + B \cdot t + C \cdot t^2/2 + D \cdot t^3/3 - E/(2 \cdot t^2) + G$$

Coefficients A to H can be found in the appendix for each component.

The Standard Enthalpy of formation  $\Delta H_{f,i}^0(T)$  and Entropy  $\Delta S_i^0(T)$  for each component at  $T = 593.15 \text{ K}$  are:

Enthalpy, kJ/mol			
H2	CO2	CH4	H2O
8.61	-380.94	-62.13	-231.75

Entropy, J/(mol*K)			
H2	CO2	CH4	H2O
150.74	242.74	215.39	212.63

The total Standard Enthalpy of formation and Entropy is:

$v_i > 0$  as product and  $v_i < 0$  as educt for component  $i$

$$\Delta H_R^0(T) = \sum_i v_i \cdot \Delta H_{f,i}^0(T) = -179.13 \text{ kJ/mol}$$

$$\Delta S_R^0(T) = \sum_i v_i \cdot \Delta S_i^0(T) = -205.05 \text{ J/(mol K)}$$

2. Calculate Gibb's Enthalpy  $\Delta G_R^0(T)$ :

$$\Delta G_R^0(T) = \Delta H_R^0(T) - T \cdot \Delta S_R^0(T) = -57.5 \text{ kJ/mol}$$

3. Calculate the equilibrium constant:

$$K_{eq} = e^{-\Delta G_R^0(T)/RT} \left\{ p_0^{\sum v_i} \right\} = 1.16 \cdot 10^5 \text{ 1/bar}^2$$

The term in the braces is '1' with  $p_0 \approx 1 \text{ bar}$ , but is retained to keep the equation dimensionally correct.

$K_{eq} \gg 1$ , equilibrium of reaction is on the product side

4. Reached the reaction its equilibrium state? In equilibrium  $K_p = K_{eq}$ .

$$K_p = \prod_i p_i^{v_i} = \frac{p_{CH_4} \cdot p_{H_2O}^2}{p_{CO_2} \cdot p_{H_2}^4} = \frac{2.513 \text{ bar} \cdot 2.198^2 \text{ bar}^2}{0.058 \text{ bar} \cdot 0.231^4 \text{ bar}^4} = 7.35 \cdot 10^4 \text{ 1/bar}^2$$

$K < K_{eq} \rightarrow$  reaction reached not equilibrium (due to the low temperature of  $320^\circ\text{C}$ , where the catalyst do not show a high activity).

- iii. Equilibrium constant and methanation with steam:** The catalyst starts to deactivate due to carbon deposition. A countermeasure is the injection of steam into the reactor. How does the steam affect the maximum conversion rate of carbon dioxide? Show it in a qualitative way with the equation  $K_p = \prod_i p_i^{v_i}$  for component  $i$ .

$K_{eq}$  is the maximum achievable value of  $K$  at given temperature  $T$  and for the given methanation reaction. If steam is added, the partial pressure of water  $p_{H_2O}^2$  in the  $K_p$  - equation is increasing and with that the  $K$ -value for the same conversion rate of carbon dioxide. Thus the maximum  $K$ -value  $K_{eq}$  is reached with lower conversion rate.

$$K_p = \prod_i p_i^{v_i} = \frac{p_{CH_4} \cdot p_{H_2O}^2}{p_{CO_2} \cdot p_{H_2}^4}, \text{ for}$$

$C_{CO_2} = \text{const.}$  and  $p_{H_2O}^2 \uparrow \rightarrow K_p \uparrow$ , while  $K_{eq} = \text{const.}$  (at fixed temp.)

For increasing CO<sub>2</sub> conversions the K-value reaches faster the value of K<sub>eq</sub>, where the conversion reaches its thermodynamic limit C<sub>CO<sub>2</sub></sub><sup>eq</sup>. Thus:

$$C_{CO_2}^{eq,steam} < C_{CO_2}^{eq}$$

The maximum possible conversion rate of carbon dioxide is decreasing with the addition of steam. Hence the addition of steam in order to protect the catalyst against deactivation should be as low as possible.

- iv. Equilibrium constant and operational conditions in the reactor:** How can the effect of steam addition be compensated? Show it in a qualitative way with the equation  $K = \prod_i p_i^{v_i}$  for components i at constant temperature T<sub>meth</sub>.

The decreasing conversion rate of CO<sub>2</sub>, due to steam addition can be compensated by the increase of pressure in the reactor (p<sup>low</sup> < p<sup>high</sup>):

$$K = \prod_i p_i^{v_i} = \frac{p_{CH_4} \cdot p_{H_2O}^2}{p_{CO_2} \cdot p_{H_2}^4} = \frac{p x_{CH_4} \cdot p^2 x_{H_2O}^2}{p x_{CO_2} \cdot p^4 x_{H_2}^4}$$

Due to the higher degree of the reactant hydrogen (4<sup>th</sup> degree) in comparison with the other components, the denominator of K is increasing stronger than the numerator for constant carbon dioxide conversion. Thus K is decreasing for the same CO<sub>2</sub> Conversion.

$$K_p^{low} > K_p^{high}$$

This leads to a higher maximum CO<sub>2</sub> Conversion C<sub>CO<sub>2</sub></sub><sup>eq</sup> (explained in task iii).

$$C_{CO_2}^{eq,p^{low}} < C_{CO_2}^{eq,p^{high}}$$

## Appendix:

### NIST – Database

#### Correlations:

$$H^\circ - H^\circ_{298.15} = A*t + B*t^2/2 + C*t^3/3 + D*t^4/4 - E/t + F - H$$
$$S^\circ = A*\ln(t) + B*t + C*t^2/2 + D*t^3/3 - E/(2*t^2) + G$$

$H^\circ$  = standard enthalpy (kJ/mol)  
 $S^\circ$  = standard entropy (J/mol\*K)  
t = temperature (K) / 1000.

$$T0 = 298.15K$$

#### Hydrogen

$$\Delta_f H^\circ_{\text{gas}}(T0) = 0.0 \text{ kJ/mol}$$

Temperature (K)	298. - 1000.	1000. - 2500.	2500. - 6000.
A	33.066178	18.563083	43.413560
B	-11.363417	12.257357	-4.293079
C	11.432816	-2.859786	1.272428
D	-2.772874	0.268238	-0.096876
E	-0.158558	1.977990	-20.533862
F	-9.980797	-1.147438	-38.515158
G	172.707974	156.288133	162.081354
H	0.0	0.0	0.0
Reference	<a href="#">Chase, 1998</a>	<a href="#">Chase, 1998</a>	<a href="#">Chase, 1998</a>
Comment	Data last reviewed in March, 1977; New parameter fit October 2001	Data last reviewed in March, 1977; New parameter fit October 2001	Data last reviewed in March, 1977; New parameter fit October 2001

### Carbon dioxide

$$\Delta_f H^\circ_{\text{gas}}(T_0) = -393.52 \text{ kJ/mol}$$

Temperature (K)	<b>298. - 1200.</b>	<b>1200. - 6000.</b>
A	24.99735	58.16639
B	55.18696	2.720074
C	-33.69137	-0.492289
D	7.948387	0.038844
E	-0.136638	-6.447293
F	-403.6075	-425.9186
G	228.2431	263.6125
H	-393.5224	-393.5224
Reference	<a href="#">Chase, 1998</a>	<a href="#">Chase, 1998</a>
Comment	Data last reviewed in September, 1965	Data last reviewed in September, 1965

### Methane

$$\Delta_f H^\circ_{\text{gas}}(T_0) = -74.87 \text{ kJ/mol}$$

Temperature (K)	<b>298. - 1300.</b>	<b>1300. - 6000.</b>
A	-0.703029	85.81217
B	108.4773	11.26467
C	-42.52157	-2.114146
D	5.862788	0.138190
E	0.678565	-26.42221
F	-76.84376	-153.5327
G	158.7163	224.4143
H	-74.87310	-74.87310
Reference	<a href="#">Chase, 1998</a>	<a href="#">Chase, 1998</a>
Comment	Data last reviewed in March, 1961	Data last reviewed in March, 1961

Water (gaseous)

$$\Delta_f H^\circ_{\text{gas}}(T_0) = -241.83 \text{ kJ/mol}$$

Temperature (K)	<b>500. - 1700.</b>	<b>1700. - 6000.</b>
A	30.09200	41.96426
B	6.832514	8.622053
C	6.793435	-1.499780
D	-2.534480	0.098119
E	0.082139	-11.15764
F	-250.8810	-272.1797
G	223.3967	219.7809
H	-241.8264	-241.8264
Reference	<a href="#">Chase, 1998</a>	<a href="#">Chase, 1998</a>
Comment	Data last reviewed in March, 1979	Data last reviewed in March, 1979

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