Exercise 4 – Methanol Synthesis

In a methanol plant natural gas is reformed into synthesis gas (H₂, H₂O, CO and CO₂) which reacts to methanol and is distilled to high purity. This exercise will be limited to the reaction section, taking a closer look on the synthesis loop.

Question 1 – Topology

Synthesis gas enters the synthesis section of a methanol plant, and is first cooled before water is removed in a gas/liquid separator (Sep1). The liquid in the separator is pumped out by a pump (Pump1, with Pump2 on standby), and further downstream the liquid level is controlled using a level controller (LC1). In case the separator is close to fully drained there is a loop from the pump outlets back into the separator to ensure no gas flows through the pumps, controlled by a flow controller (FC). The gas from the separator top outlet is compressed (Comp1) from 30 to 80 bar, and has a loop back to the first cooler that the anti-surge controller (ASC1) opens in the case of compressor surge. Before it enters the reactors (Reactor 1 & 2), the compressed syngas is preheated by hot gas (in HEx) from the reactor outlets. The reactors are kept at constant temperature by pressurized water on the shell side, which boils from the exothermic reactions happening inside the catalyst-filled tubes. Out of the reactors the reacted gas runs through the inlet heat exchanger and two coolers (Cooler 1 & 2). These coolers condense water and methanol in the gas, which is separated from the gas in a second gas/liquid separator (Sep2). Gas out of the scrubber is split to purge and recycle. The purge gas is used elsewhere in the process, and is removed to keep inert gases from building up in the recycle loop. The recycle compressor (Comp2) compresses the recycle gas back up to 80 bar, before it is sent back to the reactors. The recycle compressor also has a flow back to the coolers, which the anti-surge controller (ASC2) opens in the case of compressor surge. The separator liquid level is controlled using a level controller (LC2). Condensed raw methanol (methanol, water and trace amount of by-products) is sent to further processing by distillation.

- Sketch the topology of the methanol synthesis section.

Figure 1: A flowsheet of the methanol synthesis loop.
**Question 2 - Model equations**

The methanol formation is highly exothermic, and the reactor temperature must be controlled to avoid catalyst deactivation and unwanted side reactions. Commonly a boiling water reactor (BWR) is applied, with multiple catalyst filled tubes surrounded by pressurized water. A BWR unit is similar to a shell and tube heat exchanger, with reaction on the tube side and boiling water on the shell side. By adjusting the pressure on the shell side, one regulates the boiling temperature and consequently the reactor temperature. Reaction heat from the tubes is what boils the water, and the resulting steam is sent to a medium pressure turbine.

a) **Write the generic component and energy balance equations for the reactor tube and shell side.**

Assume only liquid water in the inflow and steam flowing out of the shell side, and include a reaction term (\( \bar{n}_j \)) for formation of steam according to:

\[
\mathrm{H_2O \ (l)} \xrightarrow{\text{heat}} \mathrm{H_2O \ (g)}
\]

b) **How does this simplify your equations for species water (W) and steam (ST)?**

Often one prefers to represent the model in terms of the temperature (\( \frac{dT}{dt} \)) instead of the enthalpy (\( \frac{dH}{dt} \)). This requires a state-space transformation from enthalpy to temperature.

c) **Perform the simplifications on the energy balance as shown in chapter 9.4 - Common reactive systems in ABC lecture notes [1, p. 114] to get a time differential of temperature instead of enthalpy.**

As molar flows (\( \bar{n} \)) and enthalpy flows (\( \bar{H} \)) are difficult to measure, we usually prefer simple transport laws in temperature and pressure.

d) **Write down the required transport equations from chapter 5.3 Common simple transfer laws in ABC lecture notes [1, p. 74]. Assume heat only transfers between shell and tube, without losses.**

The result should be the time derivatives that can be calculated given required constants, initial conditions, inlet and outlet temperatures and pressures.
**Question 3 – Visualization of dynamics**

In this task we will use the dynamic simulation tool K-Spice to get a visualization of the dynamic equations we have constructed.

In the synthesis step, synthesis gas (H₂, H₂O, CO and CO₂) reacts to form methanol (MeOH, or CH₃OH) according to water gas shift and methanol formation from CO₂ [2]:

\[
\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2 \\
\text{CO}_2 + 3\text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}
\]

To safely run an exothermic process we require good data for heat of reaction. The reactor model in K-Spice currently assumes that reaction heat is constant in terms of temperature. This gives respectively \( \Delta h_{\text{WGS,298K}} = -41.2 \text{ kJ/mol} \) and \( \Delta h_{\text{MeOH rx,298K}} = -49.6 \text{ kJ/mol} \) at 25 °C, which is a pretty rough assumption. For better estimates of the reaction heat we can integrate the heat capacity with respect to temperature.

**Table 1: Standard enthalpy of formation and heat capacities of the components at reference state T=298 K, P=1 atm.**

<table>
<thead>
<tr>
<th>Component</th>
<th>( \Delta h_f^{\circ} ) [kJ/mol]</th>
<th>( c_p ) [J/mol K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>-393.5</td>
<td>44.63</td>
</tr>
<tr>
<td>H₂</td>
<td>0</td>
<td>29.26</td>
</tr>
<tr>
<td>CH₃OH</td>
<td>-201.3</td>
<td>61.43</td>
</tr>
<tr>
<td>H₂O</td>
<td>-241.8</td>
<td>33.59</td>
</tr>
<tr>
<td>CO</td>
<td>-110.5</td>
<td>29.79</td>
</tr>
</tbody>
</table>

**a)**  **Assume constant heat capacities and calculate the heat of reaction for water gas shift and methanol formation at 250 °C.**

Inserting these values for heat of reaction in K-Spice can be done by right clicking the reactor vessels 30V1304A and B, going into configuration and choosing the reactions button.

Should the water supply be cut, the size of the reactor shells are designed to cool the reactor for a period of time so an emergency shutdown can be performed. The two shells each have a volume of 15 m³ and the steam drum and piping give an additional liquid volume of 10 m³. The water inside is incompressible with a density of 1000 kg/m³, and boils with a heat of vaporization, \( \Delta h_{\text{vap}} \), of 1720 kJ/kg.

**b)**  **Calculate the energy required to boil the tank dry, that is to turn the full liquid volume of water into steam.**

We can assume a total methanol production rate of 2000 kmol/h and that every produced mole of methanol comes from a mole of CO, via the simple mechanism:

\[
1 \text{ CO} \xrightarrow{\Delta h_{\text{WGS,523K}}} 1 \text{ CO}_2 \xrightarrow{\Delta h_{\text{MeOH rx,523K}}} 1 \text{ CH}_3\text{OH}
\]

**c)**  **Calculate the time it takes to boil the reactor shell dry if all heat of reaction is continually removed through boiling. Assume the liquid volumes are filled with water, and that the reactor tube volumes inside the shell are negligible.**
To see this result in K-Spice, go to the Methanol reactor graphic-slide and set flow controller controller 52FICA0171 to manual with setpoint 0%. This will close the water supply of the reactor shells. Afterwards play the model in fast speed until the shell liquid levels show 0% and temperature alarms start going off.

d) **Note the time it took for the K-Spice simulation to boil all the water, and compare it to your calculation.**

The results from your hand calculations and the simulation might not match perfectly, and the heat transfer is to blame. We assumed that all heat of reaction is removed by boiling water, and this is a good assumption when all pipes are covered in water. However, as the water evaporates, part of the tubes will only have contact with steam, giving a lower heat transfer out of the reactor. This can cause the reactor temperature to rise, which can lead to a reactor runaway.


Exercise 4 – Suggested solution

Question 1 - Topology

Figure 1: Suggested topology for question 1. Controllers and valves are not shown. For simplicity, only the active pump and one reactor is shown. The control structure is not included.
Question 2 – Model equations

a) Write the generic component and energy balance equations for the reactor tube and shell side.

The mole balance of the reactor tube side is given by:

\[ \frac{\dot{n}_{i_{\text{tube}}}}{\text{change in moles with time}} = \dot{n}_{i_{\text{in}}_{\text{tube}}} - \dot{n}_{i_{\text{out}}_{\text{tube}}} + \dot{n}_{i_{\text{tube}}_{\text{generated}}} \]

Where \( i \) represents specie \( \text{H}_2, \text{H}_2\text{O}, \text{CO}, \text{CO}_2 \) or \( \text{MeOH} \).

Similarly for the shell, for the two species \( j \), Steam and Water:

\[ \dot{n}_{j_{\text{shell}}} = \dot{n}_{j_{\text{in}}_{\text{shell}}} - \dot{n}_{j_{\text{out}}_{\text{shell}}} + \dot{n}_{j_{\text{shell}}} \]

The energy balance is applied to the tubes:

\[ U_{\text{tube}} = (U_{\text{out}} + p_{\text{out}} v_{\text{out}}) - (U_{\text{in}} + p_{\text{in}} v_{\text{in}}) - q_{\text{tube}_{\text{shell}}} + (-p) V_{\text{tube}} - p V \]

Assuming constant pressure and inserting for enthalpy:

\[ \frac{\dot{H}_{\text{tube}}}{\text{enthalpy change with time}} = \frac{\dot{H}_{\text{in}}_{\text{tube}}}{\text{enthalpy flow in}} - \frac{\dot{H}_{\text{out}}_{\text{tube}}}{\text{enthalpy flow out}} - \frac{\dot{q}_{\text{tube}_{\text{shell}}}}{\text{heat flow to shell}} \]

Similarly for the shell, neglecting heat loss through external wall:

\[ \dot{H}_{\text{shell}} = \dot{H}_{\text{out}}_{\text{shell}} - \dot{H}_{\text{in}}_{\text{shell}} - \dot{q}_{\text{Shell}_{\text{Tube}}} \]

Assume only liquid water in the inflow and steam flowing out of the shell side, and include a reaction term ( \( \dot{\tilde{n}}_{j} \) ) for formation of steam according to:

\[ \text{H}_2\text{O (l)} \xrightarrow{\text{heat}} \text{H}_2\text{O (g)} \]

a) How does this simplify your equations for species water (\( W \)) and steam (\( ST \))?

As only water (\( W \)) can enter the system and steam (\( ST \)) can exit, this simplifies to:

\[ \dot{n}_{W_{\text{shell}}} = \dot{n}_{W_{\text{in}}_{\text{shell}}} + \dot{n}_{W_{\text{shell}}} \]

\[ \dot{n}_{ST_{\text{shell}}} = \dot{n}_{ST_{\text{out}}_{\text{shell}}} + \dot{n}_{ST_{\text{shell}}} \]

Where \( \dot{n}_{W_{\text{shell}}} = -\dot{n}_{ST_{\text{shell}}} \). When the reactor operates at steady state (\( \frac{dn}{dt} = 0 \)) the water flow in is equal to the generation of steam, which again is equal to the outflow of steam.
Often we wish to move from a differential in enthalpy \( \frac{dH}{dt} \) to the more measurable intensive variable temperature \( \frac{dT}{dt} \).

**b) Perform the simplifications on the energy balance as shown in chapter 8.3 - Common reactive systems in ABC lecture notes [1, p. 114] to get a time differential of temperature instead of enthalpy.**

From a) we have:

\[
\dot{H}_{\text{tube}} = \dot{H}_{\text{in, tube}} - \dot{H}_{\text{out, tube}} - q_{\text{tube, shell}}
\]

Applying a variable transform to the left side, using the differential of enthalpy at constant pressure:

\[
\dot{H}_{\text{tube}} = \frac{dH_{\text{tube}}}{dt} = \left( \frac{\partial H_{\text{tube}}}{\partial T_{\text{tube}}} \right)_{T,p} \frac{dT_{\text{tube}}}{dt} + \left( \frac{\partial H_{\text{tube}}}{\partial n_{\text{tube}}}^{T,p} \right) \frac{dn_{\text{tube}}}{dt}
\]

Inserting for partial molar enthalpies:

\[
\left( \frac{\partial H}{\partial n^{T}} \right)_{T,p} = h(T, p, n)
\]

specific heat capacity of the mixture

\[
\left( \frac{\partial H}{\partial T} \right)_{p,n} = n^{T} c_{p}(T, p, n)
\]

mole balance from a):

\[
\left( \frac{dn}{dt} \right) = \dot{n}_{\text{in}} - \dot{n}_{\text{out}} + \dot{n}
\]

the reaction term:

\[
\dot{n} = N^{T} V \dot{\xi}
\]

And heat of reaction:

\[
\Delta h = N h(T, p, n)
\]

We end up with:

\[
\dot{H}_{\text{tube}} = \frac{dH_{\text{tube}}}{dt} = n_{\text{tube}} c_{p}(T, p, n) \frac{dT_{\text{tube}}}{dt} + h(T, p, n) \left( \dot{n}_{\text{in, tube}} - \dot{n}_{\text{out, tube}} + N^{T} V \dot{\xi} \right)
\]

\[
= h^{T}(T, p, n) \dot{n}_{\text{in, tube}} - h^{T}(T, p, n) \dot{n}_{\text{out, tube}} - q_{\text{tube, shell}}
\]

Which we can simplify to the text-book equation:
\[ n_{\text{tube}} \cdot c_p(T, p, n) \frac{dT_{\text{tube}}}{dt} = \left( h^T(T_{\text{in}, p_{\text{in}}, n_{\text{in}}}) - h^T(T, p, n) \right) \hat{n}_{\text{in, tube}} \]

\[ - \left( h^T(T_{\text{out}, p_{\text{out}}, n_{\text{out}}}) - h^T(T, p, n) \right) \hat{n}_{\text{out, tube}} - \Delta h^T V \bar{\xi} - \hat{q}_{\text{tube|shell}} \]

Assuming we can use constant pure component heat capacities:

\[ h(T, p, n) = c_p'(T - T_{\text{ref}}) \]

Norming the heat capacities by moles instead of mass:

\[ m_{\text{tube}} \cdot c_p'(T, p, n) = n_{\text{tube}} \cdot c_p'(p)^T \]

the final equation becomes:

\[ n_{\text{tube}}^T \cdot c_p'(p) \frac{dT_{\text{tube}}}{dt} = c_p'(p)^T \hat{n}_{\text{in, tube}}(T_{\text{in, tube}} - T_{\text{tube}}) - c_p'(p)^T \hat{n}_{\text{out, tube}}(T_{\text{out, tube}} - T_{\text{tube}}) - \Delta h^T V \bar{\xi} - \hat{q}_{\text{tube|shell}} \]

Similarly for the shell we get:

\[ n_{\text{shell}}^T \cdot c_p'(p) \frac{dT_{\text{shell}}}{dt} = c_p'(p)^T \hat{n}_{\text{in, shell}}(T_{\text{in, shell}} - T_{\text{shell}}) - c_p'(p)^T \hat{n}_{\text{out, shell}}(T_{\text{out, shell}} - T_{\text{shell}}) - \Delta h^T V \bar{\xi} - \hat{q}_{\text{shell|tube}} \]

As molar flows (\( \hat{n} \)) and enthalpy flows (\( \hat{H} \)) are difficult to measure, we usually prefer simple transport laws in temperature and pressure.

**c)** Write down the required transport equations from chapter 3.3 Common simple transfer laws in ABC lecture notes [1, p. 74]. Assume heat only transfers between shell and tube, without losses.

Molar flow inserted for concentration and volumetric flow rate:

\[ \hat{n}_{a|b} = C_{a|b} \hat{V}_{a|b} \]

Volumetric flow is a basic flow driven by pressure differences:

\[ \hat{V}_{a|b} = -k_{a|b} V \text{sign}(p_b - p_a) \sqrt{|p_b - p_a|} \]

Conductive heat transfer:

\[ \hat{q}_{a|b} = -k_{a|b}^Q (T_b - T_a) \]
Question 3 – Visualization of dynamics

a) Assume constant heat capacities and calculate the heat of reaction for water gas shift and methanol formation at 250 °C.

First we calculate the component enthalpies at correct temperature, assuming constant $c_p$:

$$h_i(T) = h_i(T_{ref}) + \int_{T_{ref}}^{T} c_{p,i} dT = h_i(T_{ref}) + c_{p,i}(T - T_{ref})$$

Then we insert this in the reaction enthalpy:

$$\Delta h_{rx,523K} = \sum (v h)_{products,523K} - \sum (v h)_{reactants,523K}$$

For the given reactions this gives:

$$\Delta h_{WGS,523K} = -38.8 \text{ kJ mol}^{-1}$$

$$\Delta h_{MeOH,523K} = -58.0 \text{ kJ mol}^{-1}$$

Inserting these values for heat of reaction in K-Spice can be done by right clicking the reactor vessels 30V1304A and B, going into configuration and choosing the reactions button. Change the values in the heat of reaction for the two first reactions, water gas shift and methanol reaction, respectively.

![Figure 2: Reaction panel in K-Spice where reaction parameters can be given.](image)

Should the water supply be cut, the size of the reactor shells are designed to cool the reactor for a period of time so an emergency shutdown can be performed. The two shells each have a volume of 15 m³ and the steam drum and piping give an additional liquid volume of 10 m³. The
water inside is incompressible with a density of 1000 kg/m³, and boils with a heat of vaporization, \( \Delta h_{\text{vap}} \), of 1720 kJ/kg.

b) Calculate the energy required to boil the tank dry, that is to turn the full liquid volume of water into steam.

Energy required to boil all water from the shells, pipes and steam drum:

\[
\Delta H_{\text{vap}} = m \Delta h_{\text{vap}} = V \rho_{\text{water}} \Delta h_{\text{vap}} = (2 \times 15 + 10) \, \text{m}^3 \times 1000 \, \text{kg/m}^3 \times 1720 \, \text{kJ/kg} = 68.8 \, \text{GJ}
\]

We can assume a total methanol production rate of 2000 kmol/h and that every produced mole of methanol comes from a mole of CO₂, via the simple mechanism:

\[
\text{1 CO} \xrightleftharpoons{\Delta h_{\text{WGS,523K}}} \text{1 CO₂} \xrightarrow{\Delta h_{\text{MeOH rx,523K}}} \text{1 CH₃OH}
\]

c) Calculate the time it takes to boil the reactor shell dry if all heat of reaction is continually removed through boiling. Assume the liquid volumes are filled with water, and that the reactor tube volumes inside the shell are negligible.

Produced heat in reactor:

\[
\Delta H_{\text{rx,total,523K}} = \Delta h_{\text{rx,total,523K}} \eta_{\text{produced}} = (\Delta h_{\text{WGS,523K}} + \Delta h_{\text{MeOH rx,523K}}) \eta_{\text{produced}} = 53.38 \, \text{MW}
\]

Which we can use to calculate the time to boil the reactor dry:

\[
t = \frac{\Delta H_{\text{vap}}}{\Delta H_{\text{rx,total,523K}}} = \frac{68.8 \, \text{GJ}}{53.38 \, \text{MW}} = 1289 \, \text{s} = 21 \, \text{minutes and 29 seconds}
\]

To see this result in K-Spice, go to the Methanol Boiler graphic-slide and set flow controller controller 52FICA0171 to manual with OP 0%. This will close the water supply of the reactor shells.
Figure 3: The flow controller is set to manual mode with a OP of 0%. This will close the water supply, as can be seen from the grey colour of the valve.

Afterwards play the model in 10 times speed until the shell liquid levels show 0% and temperature alarms start going off. Note the time it took for the simulator to boil all the water, and compare it to your calculation.

Figure 4: After 21 minutes the shell level indicators show that they are empty and the temperature increases rapidly.

The results from your hand calculations and the simulation might not match perfectly, and the heat transfer is to blame. We assumed that all heat of reaction is removed by boiling water, and this is a good assumption when all pipes are fully covered in water. However, as the water evaporates, part of the tubes will only have contact with steam, giving a lower heat transfer out
of the reactor. This can cause the reactor temperature to rise, which can lead to a reactor runaway.