Kinetics and Reactor Modeling of Methanol Synthesis from Synthesis Gas

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History of MeOH synthesis at a glance:

- Started from 1661, developed in 1800s
- First time commercial production: from wood (1830-1920)
- 1923: BASF introduced coal based HP MeOH
- Late 1960s: MP & LP processes, Copper based catalyst

Methanol is an important final and intermediate chemical product
Reactions of MeOH Synthesis

1. \( CO + 2H_2 = CH_3OH \) \( (DH=-21.66 \text{ kcal/mol}) \)
2. \( CO_2 + 3H_2 = CH_3OH + H_2O \) \( (DH=-11.83 \text{ kcal/mol}) \)
3. \( CO_2 + H_2 = CO + H_2O \) \( (DH=+9.84 \text{ kcal/mol}) \)

- Both exothermic and exhibit reduction in volume

- Therefore: High P and Low T is in favour of synthesis

- Reactions 1 and 3 are independent and limited by thermodynamic equilibrium
Typical Commercial Catalyst Composition

- Copper oxide: 60-70%
- Zinc oxide: 20-30%
- Alumina: 5-15%

- Copper, an extremely selective catalyst, high yield, 99.5% of converted CO+CO2 is MeOH
- Shape: Tablet form, cylinders: 5.5 into 3.5 mm or 5 into 5 mm
- Reduction: 1% H2 in N2 or Methane at max. 230 °C
- Catalyst poisoning: Sulfide and Chlorine
Highlights of MeOH Synthesis

• Exothermic Reaction, Heat integration and Recovery are important feature

• Current Technologies: Heat Transfer based:
  1. ICI: Quench Reactor
  2. Lurgi: Tubular
  3. Mitsubishi: Double-Tube Heat Exchange reactor

• Trends in technology improvement: Larger capacity, improved energy efficiency

• Suitable Syngas Technology (Topsøe, Lurgi, Mitsubishi): Two step Reforming, Primary SR plus ATR

• 32 to 44 % of the energy is used for the production of MeOH
Tube cooled: Catalyst bed + heat exchangers in one vessel
Relatively lower cat. Vo
Better heat recovery
7 commercial units operating now

<table>
<thead>
<tr>
<th>Type</th>
<th>Adiabatic quench (ARC-multibed)</th>
<th>Isothermal tubular</th>
<th>Tube cooled</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas flow</td>
<td>Axial (Quenchgas : Radial)</td>
<td>Axial</td>
<td>Axial</td>
</tr>
<tr>
<td>Heat recovery</td>
<td>BFW preheat</td>
<td>MP steam</td>
<td>BFW preheat</td>
</tr>
<tr>
<td>Single train capacity</td>
<td>Up to 3,000 mtpd</td>
<td>Up to 1,500 mtpd</td>
<td>Up to 2,000 mtpd</td>
</tr>
<tr>
<td>Cost factor, reactor only</td>
<td>Low cost</td>
<td>High cost</td>
<td>Low cost</td>
</tr>
</tbody>
</table>

*Fig. 6-3*
Methanol synthesis loop – different reactor types

*Microstructured reactors, Velocys, Heatric…?*
Challenges in Conventional MeOH Technology

1. Heat Management,
   • Non-isothermal behaviour,
   • Trend: leading to different reactor configurations

2. Conversion per pass:
   – Higher T, lower Conversion, Nature of the reaction (Eq. Limitation),
   – Trend: leading to development of low temp. active catalysts
Project Scope

Offshore conversion of remote gas to methanol

Future Solution for Stranded Gas Fields?
Comparative study of two reactors

- Non isothermal packed bed reactor
- Micro-Packed Bed Reactor-Heat Exchanger
Objectives of model development:

1. To develop a model and predict the experimental data on a laboratory scale fixed bed reactor for methanol synthesis
2. Comparative performance study of fixed bed reactor and a microstructured reactor via developed models (next phase of the project)
3. COMSOL Multiphysics software package (MATLAB based) was used in this study
Fixed Bed Reactor Model

- **Model assumptions:**
  1. Pseudo-homogeneous,
     
     \[ \text{C}_g = \text{C}_s \text{ and } \text{T}_g = \text{T}_s \]

     No T and C gradient within particles

  2. 2D model: no radial velocity is considered, but dispersion and heat transfer exists in both radial and axial directions
Kinetic Rate Equations

\[ \text{CO}_2 + 3\text{H}_2 \leftrightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \quad (\Delta H = -11.83 \text{ kcal/mol}) \quad (2) \]

\[ \text{CO}_2 + \text{H}_2 \leftrightarrow \text{CO} + \text{H}_2\text{O} \quad (\Delta H = +9.84 \text{ kcal/mol}) \quad (3) \]

\[
\begin{align*}
    r_{\text{MeOH}} &= \frac{k_d \cdot p_{\text{CO}_2} \cdot p_{\text{H}_2} \cdot ((1 - (p_{\text{H}_2} \cdot p_{\text{CH}_3\text{OH}} / (p_{\text{H}_2})^3 \cdot p_{\text{CO}_2} \cdot K_{eq1} )))}{((1 + k_c \cdot p_{\text{H}_2} / p_{\text{H}_2} + \sqrt{(p_{\text{H}_2}) \cdot k_a + k_b \cdot p_{\text{H}_2}})^3)}
\end{align*}
\]

\[
\begin{align*}
    r_{\text{RWGS}} &= \frac{k_e \cdot p_{\text{CO}_2} \cdot (1 - K_{eq2} \cdot p_{\text{H}_2} \cdot p_{\text{CO}} / p_{\text{CO}_2} \cdot p_{\text{H}_2})}{(1 + k_c \cdot p_{\text{H}_2} / p_{\text{H}_2} + \sqrt{(p_{\text{H}_2}) \cdot k_a + k_b \cdot p_{\text{H}_2}})}
\end{align*}
\]
Chemical Reaction Engineering Lab

Mole fraction profiles of reactants and products from CREL, Adiabatic Plug Flow Reactor

P = 80 bara and T = 255 C

Kinetic model is in a good agreement with literature, Jakobsen et al., Computers and Chem. Eng., 26, 2002
Governing Equations, Boundary Conditions

• **Mass Balance**

\[
\frac{\partial c_i}{\partial t} + D_{er} \left( \frac{\partial^2 c_i}{\partial r^2} + \frac{1}{2} \frac{\partial c_i}{\partial r} \right) + D_{ea} \frac{\partial^2 c_i}{\partial z^2} = u_s \frac{\partial c_i}{\partial z} - \rho_B r_i
\]

• **Energy Balance:**

\[
\frac{\partial T}{\partial t} + \lambda_{er} \left( \frac{\partial^2 T}{\partial r^2} + \frac{1}{2} \frac{\partial T}{\partial r} \right) + \lambda_{ea} \frac{\partial^2 T}{\partial z^2} = u_s \rho_f c_p \frac{\partial T}{\partial z} - \rho_B (\Delta H) r_i
\]

• **Initial Conditions:**

\[
C_i = C_0 \quad \text{at all } r \text{ and } z
\]

\[
T = T_0
\]

• **Boundary Conditions (t>0):**

\[
\frac{\partial C}{\partial r} = 0 \quad \text{at } r = 0 \quad \text{and } r = R \text{ all } z
\]

\[
C_i = C_0 \quad \text{at } z = 0 \quad 0 \leq r \leq R
\]

\[
T = T_0
\]

\[
\frac{\partial T}{\partial z} = - \frac{U}{\lambda_{er}} (T - T_a) \quad \text{at } r = R \text{ all } z
\]

\[
\frac{\partial C}{\partial z} = \frac{\partial T}{\partial z} = 0 \quad \text{at } z = L \quad 0 \leq r \leq R
\]

Fixed wall T, convective flux at the exit, constant velocity along the bed (laminar)
## Reactor & Catalyst Data:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inner Tube Diameter (m)</td>
<td>0.00914</td>
</tr>
<tr>
<td>Outer Tube Diameter (m)</td>
<td>0.0127</td>
</tr>
<tr>
<td>Tube Length (m)</td>
<td>0.03</td>
</tr>
<tr>
<td>Shell Temperature (K)</td>
<td>493 - 513</td>
</tr>
<tr>
<td>Catalyst System</td>
<td>CuO/ZnO/Al₂O₃</td>
</tr>
<tr>
<td>Pellet size</td>
<td>50-200 μm</td>
</tr>
<tr>
<td>Catalyst Density</td>
<td>1250 Kg m⁻³</td>
</tr>
<tr>
<td>Bulk Void Fraction</td>
<td>0.5</td>
</tr>
</tbody>
</table>

## Synthesis gas composition (vol%):

<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>0.65</td>
</tr>
<tr>
<td>CO</td>
<td>0.25</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.05</td>
</tr>
<tr>
<td>N₂</td>
<td>0.05</td>
</tr>
</tbody>
</table>

## Model Coefficients

- **Axial Dispersion**: Wen & Fan, 1975
- **Radial Dispersion**: De Ligny et al., 1970
- **Axial Gas Thermal Conductivity**: Yagi et al., 1960
- **Radial Gas Thermal Conductivity**: Froment & Bischoff, 1979
- **Overall Heat Coefficient**: Froment & Bischoff, 1979
2D Simulation of the reactor

P=80 bars, syngas flow= 250 nml/min

The wall temp. strongly affects bed temperature distribution
2D Simulation of the reactor

Variation of CO conversion with gas velocity

P=80 bars, T max= 255 C
2D Simulation of the reactor

The non-isothermal behaviour in Fixed Bed Reactor for exothermic reaction

P=80 bars, T max= 255 C, Flow= 250 nml/min
2D Simulation of the reactor

- Hot spot moves down the reactor length with increasing the flow
- Temperature distribution heavily affects the reactor performance

Syngas Flow= 250 nml/min
Syngas Flow= 500 nml/min
Syngas Flow= 750 nml/min
Conclusion

- The kinetic model is in a good agreement with similar published work.
- The 2D model considers both axial and radial dispersion of heat and mass and consequently provides a good tool for lab scale studies.
- With increasing gas velocity, CO conversion decreases and hot spot moves down the reactor.
- The well known thermal behaviour of exothermic reactions in fixed bed reactors could be predicted by this model.
- Based on the knowledge gained in this work, the next step of this research is to build up a model for methanol synthesis in a microstructured heat exchanger - packed bed reactor.
Thanks for your kind attention!