Process Design and Heat Integration for the Power-to-Methanol Route

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Outline

1. Introduction
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4. Heat Integration
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1. Introduction

Background: **Renewable Energy Storage with Liquid Fuels**

- European Commission goals to reduce greenhouse gas emissions by 80% below 1990 levels by 2050, 20% by 2020 (Energy Roadmap 2050).

- Varying nature of renewable sources causes time imbalance between production and consumption.

- Need for energy storage at different time-scales:
  - Second and minute scale for frequency regulation
  - Inter-seasonal scale: Power-to-gas, power-to-fuel
1. Introduction

Power-to-Methanol route

I. CO₂ Capture
II. H₂O/CO₂ Co-Electrolysis
III. Methanol Synthesis and Purification

Methanol as liquid energy carrier ➔
(22.7 MJ/kg)
- easy and cheap long term energy storage
- converted to electricity or fuel use
- CO₂ neutral, if renewable sources are used

Léonard et al., 2015. Electricity storage with liquid fuels in a zone powered by 100% variable renewables, IEEE 978-1-4673-6692-2.
2. Model Description

### H$_2$O/CO$_2$ Co-Electrolysis model

1. $\text{H}_2 + \text{CO}_2 \rightarrow \text{H}_2\text{O} + \text{CO}$

2. $\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2} \text{O}_2$
   $\text{CO}_2 \rightarrow \text{CO} + \frac{1}{2} \text{O}_2$

3. $\text{H}_2 + \text{CO}_2 \rightarrow \text{H}_2\text{O} + \text{CO}$

- Redlich-Kwong-Soave equation of state
- Solid Oxide Electrolysis Cell at 850°C and 1.013 bar
- $\text{H}_2\text{O}/\text{CO}_2/\text{H}_2$ feed ratio: 100/45/10
- Operation at thermoneutral point
- $\text{H}_2\text{O}$ and $\text{CO}_2$ utilization factor: 70%
2. Model Description

Methanol Synthesis model

\[
\begin{align*}
\text{CO}_2 + 3 \text{H}_2 & \leftrightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \\
\text{CO}_2 + \text{H}_2 & \leftrightarrow \text{CO} + \text{H}_2\text{O}
\end{align*}
\]

Methanol Synthesis usually reaches low per-pass conversions:
- Strongly exothermic reaction (low temperature required)
- Need for high pressure (~50 bar)
- High recycle flow for industrial processes

**Internal Condensation Reactor**
- Internal liquid condensation and gas recirculation
- Leads to 100% conversion
- Small scale applications allow better heat management

_Bos and Brilman, 2014. DOI:10.1016/j.cej.2014.10.059_
2. Model Description

Methanol Synthesis model

1. Methanol Synthesis
- Redlich-Kwong-Soave equation of state
- Simplified Reactor (equilibrium is achieved): 250°C; 50 bar
- Side reactions neglected
- Condenser: 25°C; 50 bar
- Recycle (2% purge)

2. Methanol Purification
- NRTL model
- Distillation column with 11 stages
- 1.013 bar
2. Model Description

Sub-processes linked through 2 stages-compression with intermediate cooling.

Models of the two parts are validated separately, according to experimental data available.
3. Results

- The H/C ratio achieved in the produced syngas is equal to 2.4. The electrical energy consumed by the electrolyser 5584 kW, almost 53% of the sub-process total energy demand.

- Results are validated with a relative error of 3.75%.

- Methanol synthesis reactor reaches per-pass conversion of hydrogen up to 22.4% and overall conversion of 99.8%.

- Methanol productivity is 34.2 kmol/hr (about 1 ton/hr), with 97.7% purity.
4. Heat Integration

Pinch Point Analysis

- Problem targeting:
  6 cold streams – 7 hot streams
- Minimum approach $\Delta T$: 20°C
- Pinch point: 245.2°C
- Minimum utility requirements
  Hot: 935.6 kW
  Cold: 1563.3 kW

Heat Exchanger Network

- Maximum energy recovery design saves 73% of energy required.
- Above the pinch:
  3 HE and 5 hot utilities
- Below the pinch:
  9 HE and 6 cold utilities
4. Heat Integration

Economic Evaluation

- Overall Heat Transfer Coefficient (U) preliminary estimation for each exchanger.
- Total Heat Transfer Area (A) estimation: 2657 m².
- Bare module cost ($C_{BM}$) estimation using method described by Turton et al. (2013), updated with CEPC Index (April 2015): 6,292,835 €.

\[
Q = U \cdot A \cdot \Delta T_{LMTD} \cdot f
\]

\[
A_{tot} = \Sigma \left[ \frac{Q_i}{\Delta T_{LMTD,i} \cdot U_i} \right]
\]

\[
C_{BM} = C_0 \cdot (B_1 + B_2 f_m f_p)
\]

Efficiency Assessment

- Process efficiency without HEN: 51.4%.
- Process efficiency with HEN: 70.8%.

\[
\eta = \frac{HHV_{out\_Met} - HHV_{in\_H2}}{Q_{in} + P_{el} + P_{comp}}
\]

<table>
<thead>
<tr>
<th>Inlet H₂ HHV $(HHV_{in_H2})$</th>
<th>Outlet Methanol HHV $(HHV_{out_Met})$</th>
<th>Electrical Power Input $(P_e)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.795</td>
<td>7.053</td>
<td>7.316</td>
</tr>
</tbody>
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<tr>
<th>Hot Utilities without HEN $(Q_{in})$</th>
<th>Hot Utilities with HEN $(Q_{in})$</th>
<th>Compression Power Input $(P_{comp})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.265</td>
<td>0.936</td>
<td>0.590 MW</td>
</tr>
</tbody>
</table>
5. Conclusions and Further Work

- An efficient process for CO$_2$-neutral methanol production is proposed as long-term energy storage.

- Production rate of 1 ton$_{\text{CH}_3\text{OH}}$/hr, corresponding to typical decentralized energy storage.

- Benefits from a heat exchangers network design, but high capital cost needed.

- Solid Oxide cells allow both electrolysis and fuel cell mode.

- A preliminary model is proposed, some further improvements are required:
  - Use of recycled H$_2$ for the electrolyser
  - Pressurized electrolyser
  - Build a detailed reactor to implement methanol synthesis kinetics

- Integration of carbon capture (Léonard, 2014) in the efficiency assessment.
Thank you for your attention!

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