The Methanol Synthesis past and future

John Bøgild Hansen - Haldor Topsøe
International Methanol Conference
Taastrup – May 10, 2017
We have been committed to catalytic process technology for more than 70 years

- Founded in 1940 by Dr. Haldor Topsøe
- Revenue: 700 million Euros
- 2700 employees
- Headquarters in Denmark
- Catalyst manufacture in Denmark, China and the USA
Topsøe methanol technology and catalyst milestones

- SMK
- 1st methanol plant
- 1969

- MK-101
- CMD revamp concept
- 1986

- MK-121
- Two step reforming
- 1992

- MK-151 FENCE
- World scale plant
- 2000

- 2 * 5000 MTPD scale plant
- 2009

- 2015
Topsoe methanol plants
Since 2000

Number of plants: 40
Accumulated capacity, MTPD: 97,075
Number of catalyst charges: 168
Methanol market share
Awarded capacity 2003-2014
FENCE™ technology

- Optimising sintering barriers
- Cu crystals separated by picket fence of metal oxides
- The FENCE™ technology inhibits sintering
Industrial benefits

- Increased loop efficiency
  - Production gain
  - Increased carbon efficiency
  - Lower energy consumption
- Longer catalyst lifetime
  - Less replacements
  - Increased plant availability

Statoil, Norway, 2500 MTPD
28.8 GJ/MT => 69 % efficiency

MK-151 FENCE™

Days on Stream
Catalyst activity

MK-151 FENCE™
MK-121
MK-101

Statoil, Norway, 2500 MTPD
28.8 GJ/MT => 69 % efficiency
Reformers for Methanol Plant utilising CO₂

\[ \frac{3}{4} \text{CH}_4 + \frac{1}{2} \text{H}_2\text{O} + \frac{1}{4} \text{CO}_2 = \text{CH}_3\text{OH} \]
Methanol from sustainable sources
BioDME Black Liqour to Green DME Demo
Wood to Gasoline
DOE Project

Green Gasoline from Wood Using Carbona Gasification and Topsoe TIGAS Processes
The Active Site of Syngas Catalyst

Cu(200), \(d=0.18\text{nm}\)
Cu(111), \(d=0.21\text{nm}\)
ZnO(011), \(d=0.25\text{nm}\)
ZnO(012), \(d=0.19\text{nm}\)

\(\text{Cu(111)}\)

Cu is metallic when catalyzing
- WGS
- MeOH synthesis
- MeOH reforming

Catalyst dynamic
- Number of active sites depends on conditions

1.5mbar, 220°C
1.5mbar, \(\text{H}_2/\text{H}_2\text{O}=3/1\), 220°C
Conversion of methanol as function of CO$_2$ content in stoichiometric gas
**Fuel Cell and Electrolyser**

**SOFC**

\[ 
\text{H}_2 + 2\text{O}^2- \rightarrow \text{H}_2\text{O} + 2\text{e}^- \\
\frac{1}{2}\text{O}_2 + 2\text{e}^- \rightarrow \text{O}^2- 
\]

**SOEC**

\[ 
\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{O}^2- \\
\text{O}^2- \rightarrow 2\text{e}^- + \frac{1}{2}\text{O}_2 
\]

**H}_{2} + \text{CO} + \text{O}_2 \xleftrightarrow{\text{SOFC}} \text{H}_2\text{O} + \text{CO}_2 + \text{electric energy (}\Delta\text{G}) + \text{heat (T}\Delta\text{S})

\[ 
\text{H}_2 + \text{O}_2 \xleftrightarrow{\text{SOEC}} \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 
\]
Methanol
From CO₂ and Steam

Water

CO₂

SOEC

Oxygen

Water

SOEC

Oxygen

Methanol

Separator

Methanol

Purge

Recycle
Reactor volume and byproducts as function of CO$_2$ converted in SOEC

![Graph showing reactor volume and byproducts as function of CO$_2$ converted in SOEC. The graph plots reactor volume relative percentage and byproducts relative percentage against percent CO$_2$ through SOEC. As the percent CO$_2$ increases, the reactor volume decreases while the byproducts increase.]
Synergy between SOEC and fuel synthesis
Efficiencies electricity to MeOH = 76-79 % possible
EUDP project
50 kW SOEC and 10 Nm³/h methane

Participants:
- Haldor Topsøe A/S
- Aarhus University
- HMN Naturgas
- Naturgas Fyn
- EnergiMidt
- Xergi
- DGC
- PlanEnergi
- Ea Energianalyse

Coordinator:
- HALDOR TOPSØE

Duration:
- June 2013 - September 2017

Project sum:
- 5.3 mio €

Location:
- Foulum
Methanation and SOEC at Foulum
Production vs hours on stream. 3.1 kWh/Nm³ H₂
Results from Foulum Methanator

Temperature profile in Methanator
## Average gas compositions

<table>
<thead>
<tr>
<th>Position</th>
<th>CH₄</th>
<th>CO₂</th>
<th>N₂</th>
<th>H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biogas</td>
<td>56</td>
<td>43</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>Exit 1ˢᵗ stage</td>
<td>94.58</td>
<td>0.27</td>
<td>0.91</td>
<td>4.23</td>
</tr>
<tr>
<td>Product gas</td>
<td>97.69</td>
<td>0.00</td>
<td>0.95</td>
<td>1.36</td>
</tr>
</tbody>
</table>
GreenSynFuel Project
Mass Flows in Wood to MeOH

1000 tons Wood
262 tons Oxygen

704 tons CO₂
523 tons MeOH

59 % LHV efficiency
Mass Flows in Wood + SOEC to MeOH

1000 tons Wood
782 tons Oxygen
141 MW electricity
1053 tons MeOH

71 % LHV efficiency
**Efficiencies**
Stand alone wood gasifier and gasifier plus SOEC

<table>
<thead>
<tr>
<th>LHV Efficiency %</th>
<th>Wood Gasifier alone</th>
<th>Wood gasifier Plus SOEC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>59.2</td>
<td>70.8</td>
</tr>
<tr>
<td>District Heat</td>
<td>22.6</td>
<td>10.8</td>
</tr>
<tr>
<td>Total</td>
<td>81.8</td>
<td>81.6</td>
</tr>
</tbody>
</table>
Conclusions

• Haldor Topsøe is a major player within the methanol industry
• CO₂ is already today used to enhance methanol production based on natural gas steam reforming
• Very efficient methanol plants based on power, steam and CO₂ is possible via SOEC
• Co-electrolysis offers the opportunity to reduce methanol synthesis catalyst volumes by a factor around 5
• Coupling SOEC with biomass gasification can double the biomass potential by converting excess carbon.
To find out more or get in contact

www.topsoe.com

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