METHANOL SYNTHESIS: EFFECTS IN ONCE-THROUGH AND RECYCLE OPERATION

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Worldwide leading provider of technologies and services for enhanced catalysis R&D

- Founded in 1999
- Operative focus on catalysis
- Center for independent competitor catalyst testing
- Largest (high throughput) catalysis laboratory worldwide with > 50 reactor systems
- Financially sound and a reliable ownership structure with BASF
- Staff > 300
- International blue-chip customer base
- Facilities located in Heidelberg, Germany
WHY METHANOL SYNTHESIS?

- Large-scale chemical (> 100 MT/y)

- Pivotal hydrocarbon feedstock
  - [Carbon raw material] → Synthesis gas → MeOH
  - MeOH → MTP/MTO/Acetic acid/Formaldehyde/FC/..

- Not as simple as it seems
  - Role of water and CO₂ cofeed
  - Optimum pressure level (equilibrium vs. practicability)
  - Optimum temperature level (kinetics vs. thermodynamics)

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

\[\Delta n = -2\]
\[\Delta H_r = -91 \text{ [kJ/Mol]}\]
hte EXPERTISE IN METHANOL SYNTHESIS

- Competitive catalyst testing: Ranking, Influence of process parameters
- Catalyst Preparation + screening: Influence of catalyst synthesis parameters
- DOE: Discover correlations between process variables

- Full gas recycle: Process development
hte’s FULLY INTEGRATED WORKFLOW
“THE LAB 4.0” FOR HETEROGENEOUS CATALYSIS

hte’s fully integrated data workflow

- Planning
- Catalyst Synthesis
- Reactor Loading
- Testing
- Reporting
- Data Evaluation
- Analytics
- Sample Logistics
- Synthesis
- Planning

hte-company.com
METHANOL SYNTHESIS IN PARALLEL FIXED BED REACTORS

• Classical Catalyst screening
METHANOL CATALYST SCREENING
TEST RIG, LIBRARY LAYOUT, AND PROCESS PARAMETERS

- Parallel reactor system with 32 channels
- Two reactor blocks with independent heating, each for 16 liners
- Common pressure control
- Common feed supply

- Library of commercial and hte prepared catalysts
- Variation of catalyst amount → different GHSV at identical liner flow
AN OVERVIEW: TIME-ON-STREAM DATA

- Two catalysts: CAT1 and CAT2
- Process variables: temperature (red), CO₂ concentration (green), pressure (blue)
- Good reproducibility between identical fillings
- Catalyst 2 better than catalyst 1
EFFECT OF TEMPERATURE AND CO\textsubscript{2} COFEED

- Increasing activity with increasing reactor temperature
- Considerable increase in activity after introduction of 1 vol\% CO\textsubscript{2}
- Change from 1 to 2 vol\% CO\textsubscript{2} without effect
- Change from 2 to 4 vol\% CO\textsubscript{2} detrimental

At 1 vol\% CO\textsubscript{2} and 50 bar

At 200 °C and 50 bar
Effective gas utilization

Effective utilization of catalyst mass and reactor volume (STY)
METHANOL SYNTHESIS IN A SUB-PILOT FIXED BED REACTOR IN ONCE THROUGH MODE
FEATURES OF THE REACTOR SYSTEM

- Sub-pilot scale: reactor ID up to 25 mm, length 106 cm, > 100 ml catalyst possible
- Six individually controllable reactor heaters
- Coolable condenser with level-controlled, continuous liquid drain-off into weighted, larger product vessels
- Flow-controlled release of the hot reactor effluent or the cold condenser off-gas to the online GC analysis
- Pressure controller in major off-gas pipe
- Large set of feed gas modules in the major feed pipe
EFFECT OF GHSV AND CO$_2$ CONCENTRATION AT 220 °C

- Nearly constant MeOH formation rate between 2 and 4 vol% CO$_2$ and a GHSV between 3200-6500h$^{-1}$
- Activity mainly kinetically controlled
- Constant catalyst utilization
- CO conversion variable (~1/GHSV) $\rightarrow$ reduced feed gas utilization
On MeOH Formation and CO Conversion

- Broad peak formation rate and CO conversion around 245 °C
EFFECT OF TEMPERATURE VARIATION
AT HIGH GHSV AND LOW CO₂ CONCENTRATION

...and on formation of MeOH and side products

- Increasing formation of higher alcohols and DME at maximum MeOH formation rate
- Methanol selectivity > 99%
METHANOL SYNTHESIS IN A SUB-PILOT FIXED BED REACTOR IN RECYCLE MODE
ONCE THROUGH AND RECYCLE OPERATION

<table>
<thead>
<tr>
<th>Once through</th>
<th>Parameter</th>
<th>Recycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>User defined heater temperatures + exotherm</td>
<td>Temperature</td>
<td>User defined heater temperatures + exotherm</td>
</tr>
<tr>
<td>By pressure controller in outlet</td>
<td>Reactor pressure</td>
<td>By pressure controller in ( H_2 ) feed module</td>
</tr>
<tr>
<td>Fresh feed only</td>
<td>Feed composition and flow rate</td>
<td>Fresh and recycle feed</td>
</tr>
<tr>
<td>User defined flow rate for all feed gas modules</td>
<td></td>
<td>User defined CO feed rate</td>
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<tr>
<td></td>
<td></td>
<td>Process controlled ( H_2 ) feed rate</td>
</tr>
<tr>
<td></td>
<td></td>
<td>User defined recycle flow rate</td>
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<tr>
<td></td>
<td></td>
<td>Recycle gas composition influenced by catalyst activity</td>
</tr>
</tbody>
</table>
• Circulating gas stream with various input and output streams
• Input: fresh H$_2$ and CO
• Output
  • liquid MeOH drained off condenser
  • H$_2$, CO and gaseous MeOH purged to analytics
• Steady state inside loop: input and output streams balanced
• For CO: fresh CO feed rate = converted CO rate + purged CO rate
• Handle to adjust the CO conversion rate: temperature
• Adjust the temperature to achieve a methanol formation rate that matches the user defined CO flow rate
RECYCLE OPERATION – INITIAL RUNS

• First run: getting started
  • 220 °C, 8.5 NL/h CO fresh feed rate
  • \( \text{H}_2/\text{CO} \) consumption rate ratio: 2
  • Ratio of \( \text{H}_2 \) and CO fresh feed rates ~ 2.5
  • \( \text{H}_2/\text{CO} \) purge rate ratio: > 2

• Second run: increasing productivity
  • 230 °C, 15 NL/h CO fresh feed rate
  • Ratio of \( \text{H}_2 \) and CO fresh feed rates ~ 2.1
  • Purge rate constant, fresh feed ratio dominated by increased consumption ratio
• Third run: maximizing productivity
  • 240 °C, 22 NL/h CO fresh feed rate
  • Ratio of H₂ and CO fresh feed rates ~ 1.5
  • CO input and output stream not balanced!

• Fourth run: stabilizing productivity
  • 240 °C, 20 NL/h CO fresh feed rate
  • Recycle rate increased from 110 to 170 NL/h
  • Ratio of H₂ and CO fresh feed rates ~ 2.1
  • CO input and output stream balanced
• CO enrichment during third run at 240 °C/20 NL/h CO
• Steady CO concentration after increase of recycle flow rate
• Little change in MeOH outlet concentration between third and fourth run → thermodynamic limit!
• Higher MeOH formation rate (CO consumption rate) possible by dilution with (MeOH free) recycle gas
ONCE TROUGH VERSUS RECYCLE - METHANOL FORMATION

- MeOH formation rate of ~900 mmol/h
- High productivity achieved with little unconverted synthesis gas
- GHSV and fresh feed gas rates decoupled → high GHSV achieved by high recycle gas flow
ONCE TROUGH VERSUS RECYCLE - BYPRODUCT FORMATION

- Ethanol most important byproduct in once through
- Methane most important byproduct in recycle
- Ethanol: condensation and drain off
- Methane: transport to reactor inlet
- Methane enrichment until methane formation rate is balanced by methane output rate through purge
TRACKING OF LIQUID PRODUCT FORMATION

- Product container on balance
- Process data logged
- Good match between
  - Gravimetric Methanol formation rate of nearly 30 g/h
  - Methanol formation rate of 900 mmol/h by online GC
  - Fresh CO feed rate (20 NL/h)
- Generation of liquid samples for further offline analysis, inspection, specific tests, ...

Weight rate \([g/h]\) = \[
\frac{\text{Weight difference \([g]\)}}{\text{Time difference \([h]\)}}
\]
SUMMARY AND OUTLOOK

- Successful operation of a sub-pilot scale reactor system for methanol synthesis in once-through and recycle mode
- Recycle operation much more efficient than once through: high productivity combined with high gas utilization
- Observed activity most likely still thermodynamically limited, operation at even higher productivity (higher recycle flow, higher $H_2$ and CO fresh feed rates) well within capabilities of reactor system
- Starting point for more complex, multi-component reaction networks
THANK YOU FOR YOUR ATTENTION.