Present and future opportunities downstream gasifiers

Klas J. Andersson, Martin Skov Skjøth-Rasmussen, Poul E. Højlund Nielsen
7th International Freiberg/Inner Mongolia Conference, June 8 - 2015
Syngas conditioning and conversion

- Coal
  - Gasification
    - Sour shift
    - COS hydrolysis
    - AGR - Acid Gas Removal
      - Syngas purification

- Synthesis gas platform
  - Gasoline
  - BTX
  - Olefins
  - Propylene
  - DME
  - Formaldehyde
  - Methanol
  - Hydrogen (/CO)
  - Syngas for FT
  - Ammonia
  - SNG
Syngas conditioning and conversion

**Biomass**

- Gasification
  - Dusty tar reforming
  - Filter
  - Clean tar reforming
  - Sour shift
  - COS hydrolysis
  - AGR - Acid Gas Removal
  - Syngas purification

10-200 ppmv H$_2$S

$\text{H}_2\text{O} + \rightarrow \text{syngas}$

- Power

- Gasification
  - Hot gas filter

- Synthesis gas platform
  - Gasoline
  - BTX
  - Olefins
  - Propylene
  - DME
  - Formaldehyde
  - Methanol
  - Hydrogen (/ CO)
  - Syngas for FT
  - Ammonia
  - SNG
Ammonia history and world population

World population, billion

Ammonia, million ton (as N)

KM1

1900 1925 1950 1975 2000
Recent technology and catalyst development

- Tar reforming
- MeOH
- NH₃
- SNG - largest
- - smallest
- MTG
Process overview

- Gasification Plant Process:
  - Andritz/Carbona air blown, low pressure bubbling fluidized bed gasifier
  - Topsoe catalytic tar steam reforming
  - Gas cooling, filtration, and scrubbing

- Power Plant Process:
  - 3 Gas Engines with heat recovery and 2 Gas Boilers
Dusty tar reforming - Skive Fjernvarme I/S

- 2009: Topsoe catalyst and tar reformer operation support initiated
- 2014: Topsoe revamp of tar reformer + new larger monolith catalyst
BioDME production at LTU Biosyngas Centre - overview

The plant incl. gasification is operated by 2 operators per shift

Key operation data:
Gasification at 30bar/1050°C
Methanol synthesis at 130 bar
DME synthesis at 15 bar

Over 4 ton DME/d was reached in Sep -12
Black Liquor to Green DME Demo – Piteå/Sweden

> 3 years of operation

• New MeOH technology!
Typical methanol loop

What if we could...

~30% single pass conversion

Steam

+95% conversion
Once-through methanol synthesis

… simplify the methanol synthesis to this
Methanol Synthesis - Piteå

- Compressor
- S-guard
- MU converter
- Finishing reactor

Diagram:
- Synthesis Gas
- ZnO-based S-guard
- Cu-based S-guard
- Steam
- MeOH cat.
- Raw MeOH
Piteå BioDME pilot plant

- Production of >4 tons of DME per day demonstrated September 2013
- Production of >4.5 tons of methanol per day demonstrated November 2014
- More than 1,250,000 km cover by trucks in fleet test
- One truck has covered more than 250,000 km
- Funding for 3 more years demonstration obtained from Swedish Energy Agency Jan 2014
- BioSyngas Consortium established by Luleå Technical University
- +95% once-through conversion demonstrated in methanol synthesis for ~6 months!
Improvements in ammonia synthesis

- New ammonia synthesis catalyst
KM 111 reducibility

- XRPD for reduction of KM catalysts
- KM 111 is reduced faster
- 10 hours can be saved for reduction of KM 111

![Graph showing KM 111 reducibility](image)
KM 111 activity and stability

- Accelerated aging plot
- More than 1,200 industrial references for KM1
- Significant activity gain with KM 111
KM 111 benefits

• Basis
  • 2,100 MTPD NH₃ plant
  • 190 Bar operating pressure

• Production increase
  • Up to 1.9% Increased production
  • One week extra production per year

• Energy savings
  • 3.5 Bar reduced operating pressure

• New plants
  • Smaller converter size
  • Decreased catalyst volume
Ammonia - MUG converter in a new plant layout

<table>
<thead>
<tr>
<th>Layout</th>
<th>NH₃ Production MTPD</th>
<th>Split %</th>
<th>Loop Pressure bar g</th>
<th>Total plant Cost</th>
<th>P&amp;C figures Gcal/MT NH₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional loop</td>
<td>3500</td>
<td>0</td>
<td>196</td>
<td>100</td>
<td>6.915</td>
</tr>
<tr>
<td>MUG converter</td>
<td>2206/1294</td>
<td>37</td>
<td>196</td>
<td>98</td>
<td>6.902</td>
</tr>
</tbody>
</table>
HTS catalyst – sweet shift

Byproduct formation ($CH_4$)

Steam - Dry gas ratio

- Traditional HTS
- New HTS (Cr-free!)
HTS catalyst – sweet shift

- Experience with new HTS catalyst
  - Large industrial reference
  - Opens avenues for new ammonia plant lay-outs with reduced CAPEX and OPEX.

Industrial reference > 1 year operation

Pilot test

Cr – free!
TREMP™ technology

Methanation generates a lot of heat

\[ \text{CO} + 3\text{H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O} \quad (-\Delta H = 206 \text{ kJ/mol}) \]

Feed \((\text{H}_2\cdot\text{CO}_2)/(\text{CO}+\text{CO}_2) = 3\)

Equilibrium curve

Adiabatic reactors

Product spec. 94-98%
Benefits from TREMP process

Traditional SNG plant
- Lead reactor temperature increase
  - Inlet 288°C
  - Outlet 455°C
  - Difference 167°C
- MP saturated steam production
- High energy consumption for recycle compressor

TREMP
- Lead reactor temperature increase
  - Inlet: 250°C
  - Outlet up to 700°C
  - Difference up to 450°C
- HP SH steam production
- Energy efficient
# Topsoe SNG plants

<table>
<thead>
<tr>
<th>Client</th>
<th>Location</th>
<th>Capacity Nm$^3$/yr</th>
<th>Year awarded</th>
<th>Start-up</th>
</tr>
</thead>
<tbody>
<tr>
<td>Qinghua</td>
<td>China</td>
<td>1.4 billion</td>
<td>2009</td>
<td>2013</td>
</tr>
<tr>
<td>Gobigas (Bio-based)</td>
<td>Gothenburg, Sweden</td>
<td>19.4 million</td>
<td>2010</td>
<td>2015</td>
</tr>
<tr>
<td>Petrochina (COG)</td>
<td>Wuhai, Inner Mongolia, China</td>
<td>2 x 450 million</td>
<td>2011</td>
<td>2013</td>
</tr>
<tr>
<td>Huineng</td>
<td>Inner Mongolia, China</td>
<td>400 million</td>
<td>2011</td>
<td>2015</td>
</tr>
<tr>
<td>CNOOC (COG)</td>
<td>Shandong, China</td>
<td>160 million</td>
<td>2011</td>
<td>2013</td>
</tr>
<tr>
<td>CPI</td>
<td>Yili, Xinjiang, China</td>
<td>2 x 1 billion</td>
<td>2011</td>
<td>2016</td>
</tr>
<tr>
<td>POSCO</td>
<td>South Korea</td>
<td>700 million</td>
<td>2010</td>
<td>2015</td>
</tr>
<tr>
<td>Guizhou</td>
<td>Guizhou, China</td>
<td>290 million</td>
<td>2013</td>
<td>2015</td>
</tr>
<tr>
<td>SANJU (COG)</td>
<td>Inner mongolia</td>
<td>470 million</td>
<td>2014</td>
<td>2015</td>
</tr>
</tbody>
</table>
The world's largest SNG plant - Qinghua
From Model to Final Plant

- 16 Gasifiers
- 2 Shift Sections
- 2 AGR’s
- 1 Methanation
GoBiGas BioSNG – The world’s smallest SNG plant
Overview of project

- Wood chips
- Oxygen steam
- Clean Tar reformer
- Gasifier
- Scrubber
- Morphysorb
- Sulfur guard
- Tigas
- Off-gas
- Gasoline
- Water
Wood2Gasoline achievements

• Results:
  • +1,000 hours of tar reformer operation
  • +10,000 gallons gasoline product
  • RON = 97, MON = 86

• Independent engineer approval: October 2013

• Engine Emissions Testing
  • Toxicology review of gasoline components approved by Phillips66

• Gasoline testing by SwRI:
  • 80/20 blend found to be “substantially similar” to conventional gasoline.

• Fleet Testing:
  • 2 Camry’s (2.5 L PFI),
  • 2 Corollas (1.8 L PFI)
  • 2 F-150’s (3.5 L V6 EcoBoost®),
  • 2 Fusion’s (1.5 L EcoBoost®)
World’s largest synthetic gasoline plant

- 15,500 bpd gasoline
- Qinghua-1, China, Inner Mongolia, 2,500 bpd
- 162 t GSK-10 for Turkmengaz

Topsoe to build first large-scale plant based on TIGAS™
August 26, 2014, 11:10

A new plant in Turkmenistan will pave the way for the TIGAS™ technology – an area with a huge growth potential and importance for Topsoe’s strategic targets.

By Mads Gyldenkærne and Marianne Voigt
Take home messages…

• Opportunities in gas conditioning
  • Tar steam reforming available and industrially demonstrated for biomass gasification.

• Opportunities in syngas conversion
  • NH$_3$
    • New more active catalyst, faster reduction
    • MUG converter in loop can reduce CAPEX and increase efficiency
    • Cr–free HTS catalyst in industrial demonstration, not limited by lower S/DG
  • SNG
    • Industrially proven and several references
  • MTG
    • Industrially proven catalyst and commercially ready technology