Chemicals and Fuels from (Natural) Gas

Alfred Ecker
Life cycles of oil and gas

Is the golden age of gas coming?

- Alternative usage of gas
- Chemicals and Fuels from (Natural)gas

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- Alternative usage of gas
- Chemicals and Fuels from (Natural)gas

BP 2012, Energy Outlook 2030

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Petroleum products and natural gas consumption in Austria

- Petroleum products
- Residual fuel oil
- Heavy fuel oil
- Natural gas

Mio. tons and Mio m³

1971
2009

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Advantages and disadvantages of gas

**Advantages**
- Minimum C and CO2
- Maximum H
- Cleaner than coal and oil
- Easily to convert
- Scale up possible
- Huge Resources

**Disadvantages**
- Gaseous, low energy density (transport, storage)
- Expensive building and operating a distribution system
- Volatile - Green house gas (CO$_2$ x 20)
- No commercial direct route to liquid fuels
- Not renewable
Fischer Tropsch

ECONOMIES OF SCALE

GTL Cost vs. Capacity\(^{[9]}\)

\[
\frac{\text{Cost}_2}{\text{Cost}_1} = \left(\frac{\text{Capacity}_2}{\text{Capacity}_1}\right)^m
\]

Natural gas Reserves and Resources in Tera ($10^{12}$) m³

- Conv. NG
- Tight gas
- CBM
- Shale gas
- Aquifergas
- Gashydrate

Andruleit a.o; EEK 126 Jg. (2010), Heft 7/8, 277-282

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Sources of gas supply
North America versus Europe

North America

Europe

BP 2012, Energy Outlook 2030

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Natural Gas (Henry Hub) Chart in Dollar

- Alternative usage of gas
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Direct reactions of methane have no selectivity!!

\[ \text{CH}_4 + \frac{1}{2} \text{O}_2 \rightarrow \text{CO} + \text{H}_2 \]  
\[ \text{Syngas} \]

- \[ \text{C}_x \text{H}_y \text{O} \]  
- Oxygenates
- \[ \text{C}_x \text{H}_y \text{Z} \]  
- Organics

- \[ \text{CH}_4 \text{O}, \text{CH}_2 \text{O}, \text{CH}_2 \text{O}_2, \text{CO}, \text{CO}_2 \]  
- \[ \text{CH}_4 \]

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Synthesis gas a multipurpose source

- CH$_4$
- Syngas
- Methanol-Synthesis
- Fischer-Tropsch
- GTL
- MTS
- MTO
- MTC
- MTD
- Synfuels
- Olefins
- Chemicals
- DME
- IGCC
- Hydrogen
- Energy

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Reforming processes

LURGI

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World consumption of Syngas

- Ammonia 50%
- Methanol 12%
- Refineries 22%
- Oxo-alcohols, Acetic Acid, Reduction processes, Synthetic Fuels, Polycarbonates, Polyurethanes a.o. 16%
Hydrogen production in refineries

- Steam Reforming: 35%
- Partial Oxidation: 3%
- Gas Purification: 59%
- Others: 3%

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Hydrogen production costs

H. Franke, N. Schödel
Hydrogen Production Technology-Status and New Developments, Oil Gas European Magazine 2/2004, 78-84
Methanol synthesis

Natural gas
Biogas (CH4) → Reforming
Syngas → CO+ H2 → Methanol-Reactor
Solid Biomass → Gasifyer

• Alternative usage of gas
• Chemicals and Fuels from (Natural)gas
Chemical usage of Methanol

- DiMeTerphthalate: 3%
- MeMetacrylate: 4%
- Methylamine: 4%
- Methyl-halogenide: 7%
- MTBE: 7%
- Biodiesel a.o.: 18%
- Formaldehyde: 42%
- Acetic acid: 9%
- Solvent: 6%

Chemicals and Fuels from (Natural)gas

- Methanol
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- Methylamine: 4%
- MeMetacrylate: 4%
- DiMeTerphthalate: 3%

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Chemical usage

Natural gas

- LNG, pipeline
- Power generation
- Re-injection

Refinery

- Hydrogen H2
- Ammonia NH3
  - Urea
  - Nitric acid
  - Melamine
  - Ammonium nitrate

Syngas H2+CO

- Methanol CH3OH
  - Formalin
  - Acetic acid
  - MTBE
  - MTP
  - MTO

SNG

- Fischer Tropsch
  - HTFT
    - Olefins
    - Oxygenates

- DME

- Re-injection

- Alternarive usage of gas
- Chemicals and Fuels from (Natural)gas

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### Syntheses routes to olefins and fuels

**Feed: Syngas and Methanol**

<table>
<thead>
<tr>
<th>Process</th>
<th>Temperature</th>
<th>Conversion</th>
<th>Catalyst Type</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>MTO, MTP</td>
<td>400-450</td>
<td></td>
<td>Zeolite</td>
<td>UOP/Hydro, Lurgi</td>
</tr>
<tr>
<td>MTG</td>
<td>300-450</td>
<td>15-25</td>
<td>Zeolite</td>
<td>ExxonMobil, Uhde</td>
</tr>
<tr>
<td>MOGD, MTSyn</td>
<td>300-400</td>
<td></td>
<td>Zeolite</td>
<td>ExxonMobil, Lurgi</td>
</tr>
<tr>
<td>STD</td>
<td>250-280</td>
<td>30-70</td>
<td>Cu/Al2O3/Zelite</td>
<td>Haldor Topsoe, AirProducts</td>
</tr>
<tr>
<td>STG (TIGAS)</td>
<td>240-420</td>
<td>40-60</td>
<td>Bifunct/Zelite</td>
<td>Haldor Topsoe</td>
</tr>
<tr>
<td>FTTO</td>
<td>300-350</td>
<td></td>
<td></td>
<td>(BASF)</td>
</tr>
<tr>
<td>ATF, ATD, ATJ</td>
<td>400/280</td>
<td>1, 60</td>
<td>Al2O3/Zelite</td>
<td></td>
</tr>
</tbody>
</table>

**TIGAS=Topsoe Integrated Gasoline Synthesis**

- Alternative usage of gas
- Chemicals and Fuels from (Natural)gas

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Methanol to Synfuels

Methanol (MeOH)
19200 t/d *

Dehydration (Olefinprod.)

H₂O
10000 t/d

Oligomerisation

MtSynfuels Technology

Dist

Naphtha

Gas
741

MD

HT

Naphtha
877 t/d

Kerosene
MD 6961
Gasoil

*Angaben LURGI
OilGas 2/2007,p95

- Alternative usage of gas
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Fischer Tropsch process

- Natural Gas \( (\text{CH}_4) \) from low cost gas areas
- Steam Reforming
- CO\(+\)\(\text{H}_2\)
- Syngas
- \(\text{Fischer Tropsch} \) (LTFT)
- Gas recycle
- Water
- \( \text{C}_x \text{H}_y \) Wax
- Hydro-Cracking
- Jet Diesel
- Gas
- Naphtha
- MD

- Alternative usage of gas
- Chemicals and Fuels from (Natural)gas

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## Commercial FT-processes

<table>
<thead>
<tr>
<th>Process</th>
<th>Catalyst</th>
<th>Reactor</th>
<th>Syncrude composition, %M</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Olefin(a-Ol)</td>
</tr>
<tr>
<td><strong>HTFT</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SAS, Secunda</td>
<td>Fused Fe</td>
<td>Fluid.bed</td>
<td>Naphtha</td>
</tr>
<tr>
<td>(Sasol advanced Synthol)</td>
<td></td>
<td></td>
<td>Distillate</td>
</tr>
<tr>
<td>Synthol, PetroSA</td>
<td>Fused Fe</td>
<td>Fluid.bed</td>
<td>Naphtha</td>
</tr>
<tr>
<td><strong>LTFT</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SSBP, Sasolburg</td>
<td>Precip.Fe</td>
<td>Slurry bed</td>
<td>Naphtha</td>
</tr>
<tr>
<td>(Sasol slurry bed process)</td>
<td></td>
<td></td>
<td>Distillate</td>
</tr>
<tr>
<td>ARGE, Sasolburg</td>
<td>Precip.Fe</td>
<td>Fixed bed</td>
<td>Naphtha</td>
</tr>
<tr>
<td>(ARGE Ruhrchemie-Lurgi)</td>
<td></td>
<td></td>
<td>Distillate</td>
</tr>
<tr>
<td>SSBP, Qatar</td>
<td>Co-Al2O3</td>
<td>Slurry bed</td>
<td>Naphtha</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Distillate</td>
</tr>
<tr>
<td>SMDS, Bintulu</td>
<td>Co-SiO2</td>
<td>Fixed bed</td>
<td>Naphtha</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Distillate</td>
</tr>
</tbody>
</table>

- Alternative usage of gas
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GTL (CTL) capacities

- Shell MDS (1993/2000) Malaysia 14000 bpd
- PetroSA (1992) Südafrika 23000 (36000)
- Sasol/Qatar Petroleum (2007) Qatar 34000
- Shell/Qatar (2012) Qatar 70000 (140000)
- NNPC/Chevron (2013) Nigeria 34000
- (Sasol (seit 1982) Südafrika 150000, CTL)

**Conventional FT Reactors among the largest in the world**
Transportation fuels synthesis routes

Natural gas $\text{CH}_4$ → Reforming → FT-Synthesis

- MTP
- MTSyn
- Synthesis: Methanol, Alcohols
  - MOGD
  - ATD/ATF
- Oligomerisation/Hydrogenation
  - COD
- Hydrocracking

Synthetic fuels

- Alternative usage of gas
- Chemicals and Fuels from (Natural)gas

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## Synthetic diesel fuels

<table>
<thead>
<tr>
<th></th>
<th>Diesel (So)</th>
<th>FAME</th>
<th>NExBTL</th>
<th>GTL/FT</th>
<th>GTL/COD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dichte/15°C</td>
<td>830-840</td>
<td>885</td>
<td>775...785</td>
<td>770...780</td>
<td>810</td>
</tr>
<tr>
<td>Flammpunkt</td>
<td>55…65</td>
<td>&gt;100</td>
<td>&gt;55…80</td>
<td>60…70</td>
<td>95</td>
</tr>
<tr>
<td>Viskosität/40°C</td>
<td>3…4</td>
<td>4…5</td>
<td>3…3,5</td>
<td>2,5…4</td>
<td>2,8</td>
</tr>
<tr>
<td>Cloudpoint</td>
<td>0…-5</td>
<td>0…-15</td>
<td>5 …- 30</td>
<td>5…-30</td>
<td>&lt;-45</td>
</tr>
<tr>
<td>Cetanzahl</td>
<td>52</td>
<td>51</td>
<td>&gt;80</td>
<td>80</td>
<td>55</td>
</tr>
<tr>
<td>Destillation 10% Vol</td>
<td>230</td>
<td>350</td>
<td>200</td>
<td>210</td>
<td>235</td>
</tr>
<tr>
<td>50% Vol</td>
<td>270</td>
<td>350</td>
<td>290</td>
<td>270</td>
<td>250</td>
</tr>
<tr>
<td>90% Vol</td>
<td>330</td>
<td>350</td>
<td>300</td>
<td>300</td>
<td>330</td>
</tr>
</tbody>
</table>

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Why engage in advanced Jet fuels?

Alternative jet fuels must be produced (drop in fuels) to curtail future CO2 emission growth.

Electric power, fuel cells, Hydrogen, alcohols, plant oils are no practical solutions for propulsion.

Future Jet fuels from gas and Biomass are a must to meet aeronautical expectations.

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Hydrogen, Ethanol Aviation fuels

- Alternative usage of gas
- Chemicals and Fuels from (Natural)gas

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### Synthetic Aviation turbine fuels

<table>
<thead>
<tr>
<th>Specifications</th>
<th>FT/HC</th>
<th>FT/IPK</th>
<th>FT/COD</th>
<th>Bio-SPK</th>
<th>Oligo-Jet</th>
<th>JP7</th>
<th>JP8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density/15°C, kg/m³</td>
<td>756</td>
<td>760</td>
<td>779</td>
<td>753</td>
<td>781</td>
<td>779-806</td>
<td>775-840</td>
</tr>
<tr>
<td>Heating value, MJ/kg</td>
<td>44.1</td>
<td>43-44</td>
<td>&gt;43</td>
<td>44</td>
<td>43.7</td>
<td>43.5</td>
<td>42.8</td>
</tr>
<tr>
<td>Hydrogen, %M</td>
<td>15</td>
<td>&gt;14,5</td>
<td>&gt;14,5</td>
<td>15</td>
<td>14.8</td>
<td>&gt;14.4</td>
<td>&gt;13.4</td>
</tr>
<tr>
<td>Paraffins (N+Iso), %M</td>
<td>100</td>
<td>100</td>
<td>&gt;90</td>
<td>99</td>
<td>&gt;90</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aromatics, %M</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>3 bis 8</td>
<td>&lt;1</td>
<td>3</td>
<td>&gt;5</td>
<td>&lt;25</td>
</tr>
<tr>
<td>Sulfur, ppm</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1000</td>
<td>&lt;3000</td>
</tr>
<tr>
<td>Flash Point, °C</td>
<td>45</td>
<td>42-57</td>
<td>69</td>
<td>42</td>
<td>74</td>
<td>&gt;60</td>
<td>&gt;38</td>
</tr>
<tr>
<td>Freezing Point, °C</td>
<td>-51</td>
<td>&lt;-60</td>
<td>&lt;-60</td>
<td>-63</td>
<td>-78</td>
<td>-43.3</td>
<td>&lt;-47</td>
</tr>
</tbody>
</table>

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The demand for more hydrogen, chemicals and fuels increases NG consumption.

Hydrogenated petroleum products and synthetic fuels result less emissions.

The dominant players in the oil and gas industry want to monetize natural gas (transport or conversion).

The current oil price and a low gas price are the greatest chance to building up a GTC- and GTF -industry.