Overview of catalytic conversion of syngas

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Haldor Topsøe A/S
Outline of presentation
Haldor Topsøe’s involvement in production of new clean fuels and chemicals

• Background for presentation
  • Oil and gas prices
  • Energy policies

• Highlights from ongoing activities involving:
  • BioElectricity and heat
  • BioSNG
  • BioDME
  • BioGasoline
  • Power2Gas in Foulum

• Mainly small-scale biomass based activities
  • Will large scale facilities be economical?
Sustainable feedstock are already available
Syngas based routes are flexible and available!

Black liquor
Waste
Biomass

Synthesis Gas Platform
H₂ CO

Power
Bulk chemicals
Liquid fuel
Synthesis gas conversions

- MTS
- HTS
- LTS
- STG (TIGAS)
- Syngas for FT
- Methanol
- MTG/MTA (TIGAS)
- Formaldehyde
- DME
- MTG/MTA (TIGAS)
- GUU
- CO₂ wash
- Purification
- Ammonia
- Hydrogen (/CO)
- Gasoline
- Formaldehyde
- DME
- Methanol
- MTO
- MTP
- MTx
**Case 1: Skive CHP plant in Denmark**

28 MWth CHP plant operating since 2010 on wood pellets

- **Gasification Plant Process:**
  - Air blown, low pressure bubbling fluidized bed gasifier
  - Catalytic tar reforming, gas cooling, filtration, and scrubber

- **Power Plant Process:**
  - 3 Gas Engines with heat recovery and 2 Gas Boilers
  - Haldor Topsøe primarily involved in *Tar reforming*
    - Increases gas production
    - Convert polyaromatic components to an extent that allows the syngas to cool for further processing without fouling or precipitation
  - Utilize the high temperature levels from gasification for increased efficiency
Case 1: Skive CHP plant in Denmark
Challenges, improvements and performance

- Achievements today:
  - Total efficiency 84%
  - Electric efficiency: 28%
  - Heat efficiency: 56%

- Now on-stream ~7000 hr per year – Availability > 94 % of required operating hours (No heat production in summer)

- After original start-up two joint follow-up projects required to improve performance

- Dust handling is difficult and causes fouling of tar reforming catalyst

- Planned regenerations to increase on-stream factor

- Totally new reactor and catalyst design

Gas cleaning and conditioning is a challenge

Fresh  After 4-5 months of operation
Case 2: GoBiGas BioSNG production in Sweden
20 MW BioSNG plant operating since 2013/15 on wood pellets and forest residue

- Evaluation during 7 years – until 2020
  - Start-up 2013 – Grid supply Jan. 2015
- Cooperation between:
  - Göteborg Energi AB/ GoBiGas and suppliers
- Purpose to learn from the demonstration plant to enable scaling up to 100 MW in phase 2
- Evaluation of the following parameters:
  - Product quality
  - Plant performance – efficiency etc.
  - Plant availability
  - Environmental footprint
  - Maintenance needs
  - Operating costs
Case 2: GoBiGas BioSNG production in Sweden
Early perspectives…

• Plant size order of magnitude smaller than coal and coke oven gas (COG) based plants
• Complexity higher than coal based plants, and significantly more complex than COG plants
• Some technology solution less proven than those applied in coal and COG based plants
• Phase 2 - 100MW plant:
  • Cancelled!
  • Would require around 4 -5 ship loads of wood per week
  • Plant lacks the economy of scale achieved with coal based plants
• E.On granted +200 Million € by EU to build 100MW, but are hesitant to initiated project due to lack of political commitments…
Case 3: Piteå BioDME pilot plant
4 tons BioDME pilot operating since 2010 on black liquor

- Demonstration of new once-through methanol technology
- Demonstration of integrated fuel production from black liquor at paper mill
- BioDME to be demonstrated as diesel substitute
- Project partners:
Case 3: Piteå BioDME pilot plant
Project achievements

- 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 1.600.000 km cover by trucks in fleet test (1.200.000 Euro V, 200.000 Euro VI)
- One truck has covered more than 370.000 km
- BioSyngas Consortium established by Luleå Technical University
  - Focus on alternative feedstocks (PyOil)
  - Focus on alternative downstream products

1 million km
May 2013
Case 3: Piteå BioDME pilot plant
Project outlook and economy

• Paper mills are suffering in Scandinavia and North America!

• All commercial projects have been abandoned!

• Scenario with no tax on transportation fuels:
  • At present CO$_2$ & energy tax exemption for Biofuels are only applicable 1 year at a time.
  • Project finance requires min 3+10=13 year stable legal framework
  • Government has to accept an income loss, and find alternative revenue streams
  • Tax payers have to accept new taxes

On the bright side

• Successful demonstration of new once-through methanol converter

• The virtues of DME have been verified
Case 4: Wood 2 Gasoline pilot at GTI in Chicago
25 bbl/d gasoline production tested 2013 - 2014
Case 4: Wood 2 Gasoline pilot at GTI in Chicago
Wood2Gasoline achievements

• Status:
  • +1000 hours of operation
  • > 2000 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 at SwRI:
  • 80/20 blend found to be “substantially similar” to conventional gasoline

• NACE TM01-72 corrosion test by Innospec Fuel Specialties

• Fleet Testing
  • 75,000 mi using EPA SRC
  • 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®)
Case 4: Wood 2 Gasoline pilot at GTI in Chicago
Comparison to conventional gasoline and plant efficiency

Process efficiency in commercial biomass based plant

- Energy efficiency:
  - 45% input energy (biomass) converted to final products (gasoline + LPG)
  - State of the art GTL plant >90%

- Carbon efficiency
  - 32% input carbon (biomass) converted into final product (gasoline + LPG)
  - State of the art GTL plant >80%

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<th>Euro 5 specification</th>
<th>TIGAS</th>
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<tr>
<td>Research octane no</td>
<td>95°</td>
<td>&gt;93</td>
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<tr>
<td>Motor octane no</td>
<td>85°</td>
<td>&gt;83</td>
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<tr>
<td>Density at 15 degC</td>
<td>720-775 kg/m³</td>
<td>730 kg/m³</td>
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<td>Lead content</td>
<td>max. 5 wt ppm</td>
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<tr>
<td>Sulfur content</td>
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<td>Hydrocarbon type content:</td>
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<td>Olefins</td>
<td>max. 18 vol%</td>
<td>5-15 vol%</td>
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<td>Aromatics</td>
<td>max. 35 vol%</td>
<td>25-35 vol%</td>
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<tr>
<td>Benzene</td>
<td>max. 1 vol%</td>
<td>&lt; 1 vol%</td>
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*) Including ethanol (octane booster), and country dependent

Industrial plants awarded:
- 15.500 bbl. NG based (Turkmenistan)
- XX.X00 bbl. coal based (China)
Shale gas drive, and gasoline prices on a ten year horizon...

Our work was done at these conditions!
Motivation ½ - 1½ years later…

WTI Crude Oil Price
Case 4: Wood 2 Gasoline pilot at GTI in Chicago

Project economy

**Date:** Q2-2012  |  **Nominal:** $3.67  |  **Real:** $3.80  |  **Units:** Dollars Per Gallon

6.2 DKK/l +Taxes
**Fuel Cell and Electrolyser**

SOFC

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

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

SOEC

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

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

\[ \text{H}_2 + \text{CO} + \text{O}_2 \]

SOFC

\[ \text{H}_2\text{O} + \text{CO}_2 + \text{electric energy (}\Delta\text{G}) + \text{heat (T}\Delta\text{S}) \]
Biogas upgrade by means of SOEC

\[ \text{CH}_4 + \text{CO}_2 + 3\text{H}_2\text{O} + \text{El} \rightarrow 2\text{CH}_4 + \text{H}_2\text{O} + 2\text{O}_2 \]
Biogas to SNG via SOEC and methanation of the CO$_2$ in the biogas
New EUDP project
40 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:

Duration:
June 2013 -
March 2017
Project sum:
5.3 mio €
Location:
Foulum
GreenSynFuel Project
Mass Flows in Wood to MeOH

- 1000 tons Wood
- 704 tons CO$_2$
- 262 tons Oxygen
- 523 tons MeOH
- 59 % LHV efficiency
Mass Flows in Wood + SOEC to MeOH

- 1000 tons Wood
- 262 tons Oxygen
- 141 MW electricity
- 782 tons Oxygen
- 1053 tons MeOH
- 71 % LHV efficiency
CO$_2$ Electrofuel Project
Sponsored by NER

- Wood gasification to Methanol
- CO$_2$ to Methanol
- Wood to Methanol
- Biogas to SNG
- Landfill to SNG
Energy streams in Denmark 2014
Outlook for energy steams in Denmark 2050
Summary of leanings
Pro’s and Cons for bioderived fuels and chemicals

+ Syngas based technologies are available
+ Feedstock will be available for centuries
+ Partial solution to green house gas emissions
+ Plenty of room for improvement (Work for us all...)
  + Technologies far from optimized
  + No work on process intensification
+ Independency of geopolitic instabilities
  + Opportunity to become self supplying
+ The syngas route works
+ Biomass already contain high chemical complexity if recovered properly

- Feedstock may be limited in quantity locally and require additional logistics
- Transport of feedstock may not be economic over wide ranges
- Energy and carbon efficiencies are low
- Small to medium size plants miss the economy of scale
- CAPEX are equally high or higher when compared to conventional gas and oil based plants
- People will have to pay a premium
Conclusions

• Energy moves from fossil resources to sustainable resources
• The main energy resources are expected to be Wind and Biomasses
• Biomass needed as carbon resource for transport fuels and chemicals
• Surplus wind energy to be stored as fuels with carbon from biomass
• In a transition period a premium has to be paid to change to sustainable energy scenarios