
BioSNG and Power to Methane
New Development in Technology
September 19, 2017
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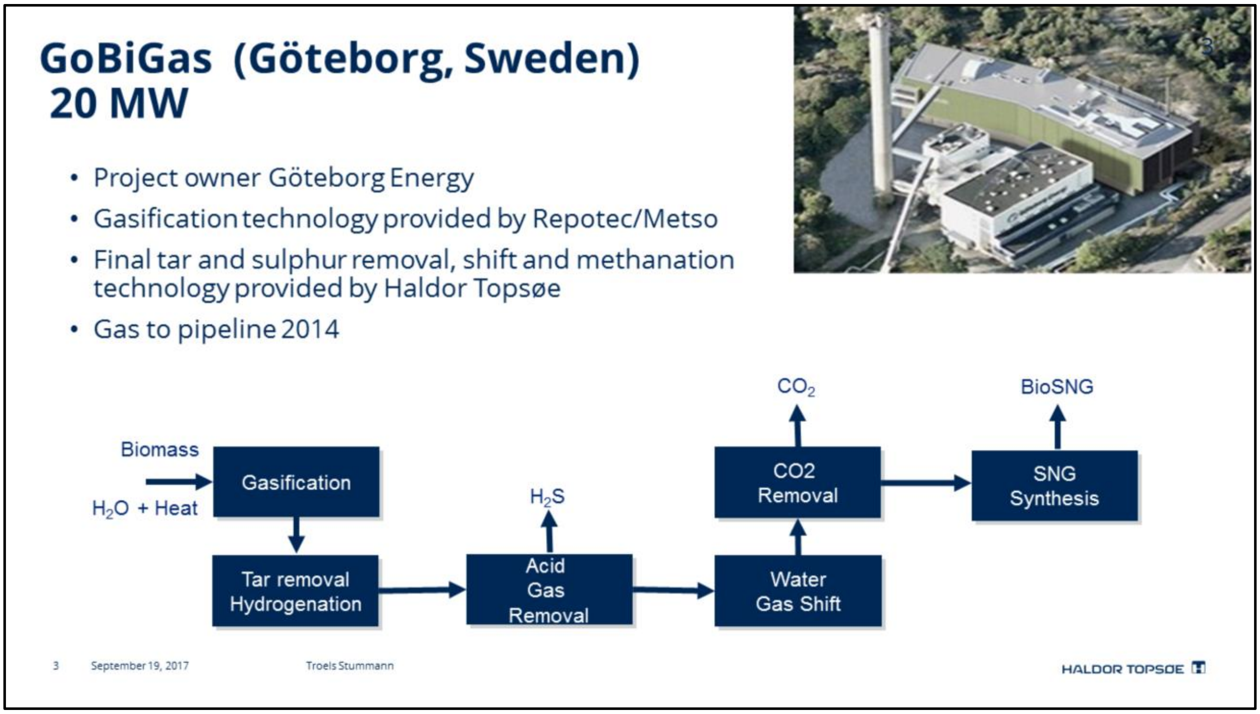
HALDOR TOPSOE

Agenda

- GoBiGas plant
- Power to Methane
- Boiling water reactor
- Tar reforming
- Conclusion
- Biogas upgrade Case



Topsoe has commercialized the first and only BioSNG plant in Sweden that converts 32 MW of wood pellets into 20 MW of BioSNG.
Plant start-up and the first SNG to pipeline in 2014

The methanation technology employed at GoBiGas is a direct scale-down of the one used in large coal-based SNG plants (i.e. adiabatic methanators in series).

GobiGas (green building)
Tar removal; wash + TSA
2 x AGR; H2S (+CO2) and final CO2 removal due to sweet shift
SNG syntheses; cascade of adiabatic reactors

While this technology is cost efficient at large scale, at smaller scale (say below 30 000 Nm3/h of product), this technology choice is too expensive. Topsoe has worked on the whole methanation section to propose a cheaper, more compact solution that cut the cost by about 30% compared to the adiabatic layout.

Divider

CO_2 removal
Adjustment of gas composition

Stoichiometric for the Methanation process

$CO + 3H_2 \leftrightarrow CH_4 + H_2O$ ($-\Delta H_0 298 = 206$ kJ/mol)

$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$ ($-\Delta H_0 298 = 165$ kJ/mol)

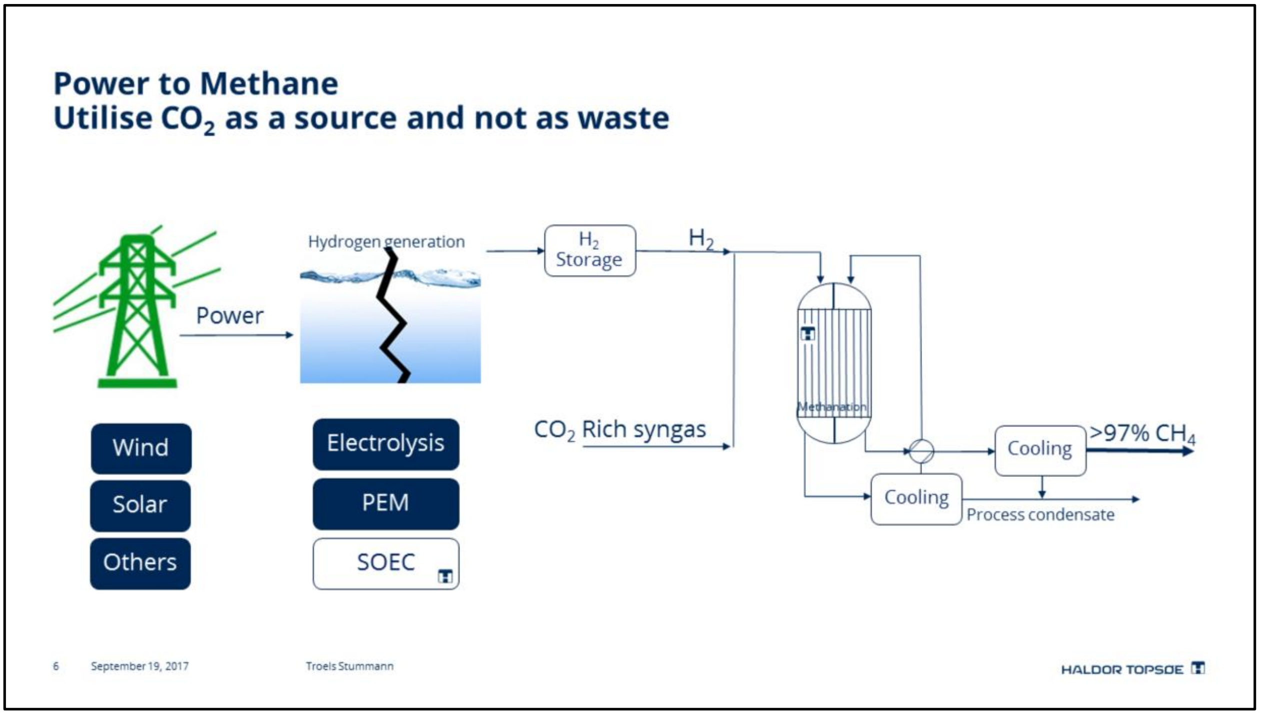
$$M_E = \frac{H_2 - CO_2}{CO + CO_2} = 3.00$$

The gas composition is adjusted by removing CO_2:

- Amine wash – high CAPEX and OPEX (reboiler duty)
- Rectisol/ Selexol will typical be too expensive for small scale plant
- Membrane – low efficiency

Regardless of the biomass origin, bio-syngases originating from gasification lack some hydrogen to meet the stoichiometric for the methanation reactions – which is needed to meet the required gas quality

For conventional SNG plants the gas composition are adjusted upstream
By shift part of the CO to H_2 and remove CO_2 in an AGR unit..
Available CO2 removal technology:
Amine wash – high energy consumption to reboiler
Rectisol/ Selexol will typical be too expensive for small scale plant
Membrane – typical low efficiency (high slip of syngas)

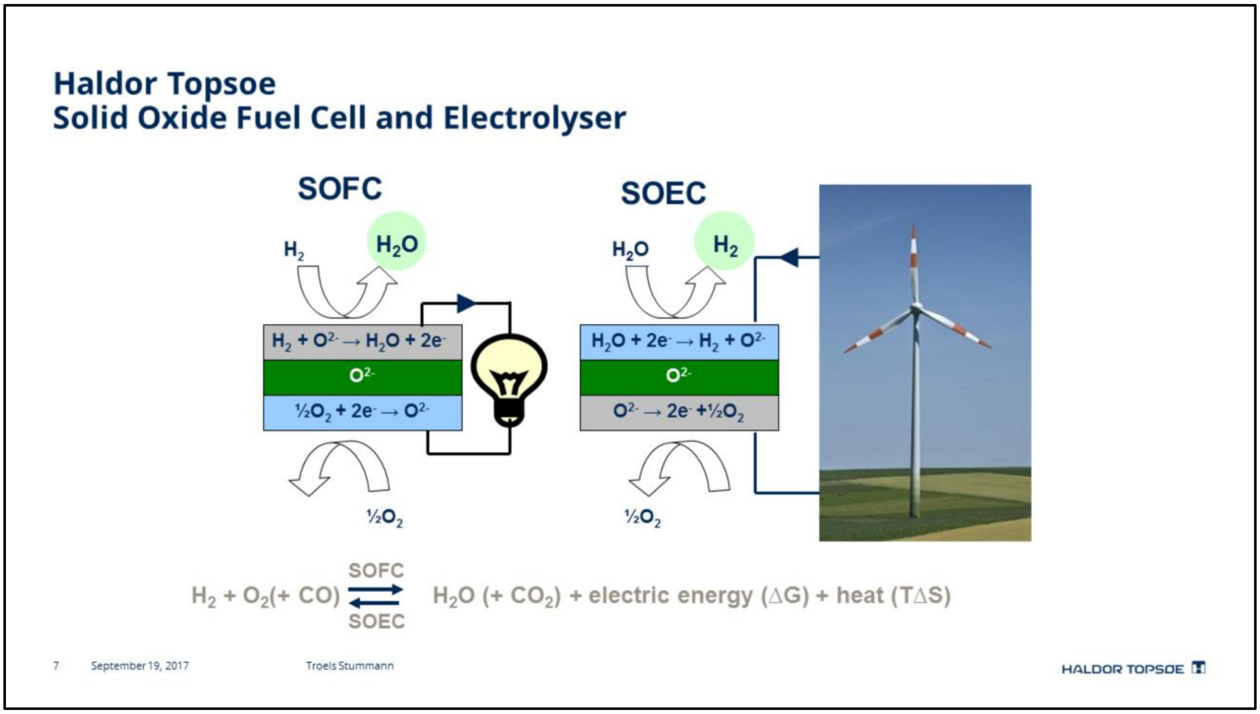


Electrolysis : alkaline
PEM: Polymer electrolyte membrane
SOEC Solid oxide electrolyser cell

Another option is to inject the required amount of hydrogen directly in the syngas thus avoiding water gas shift and the AGR unit.
Hydrogen can be produced by water electrolysis (alkaline / PEM / SOEC)
The produced oxygen can be utilized in an oxygen blown gasifier.

This approach is called Power to Methane (PtM) and can use cheap excess electricity from renewable energy sources (solar / wind) to convert it into BioSNG, that are send to the natural gas network.

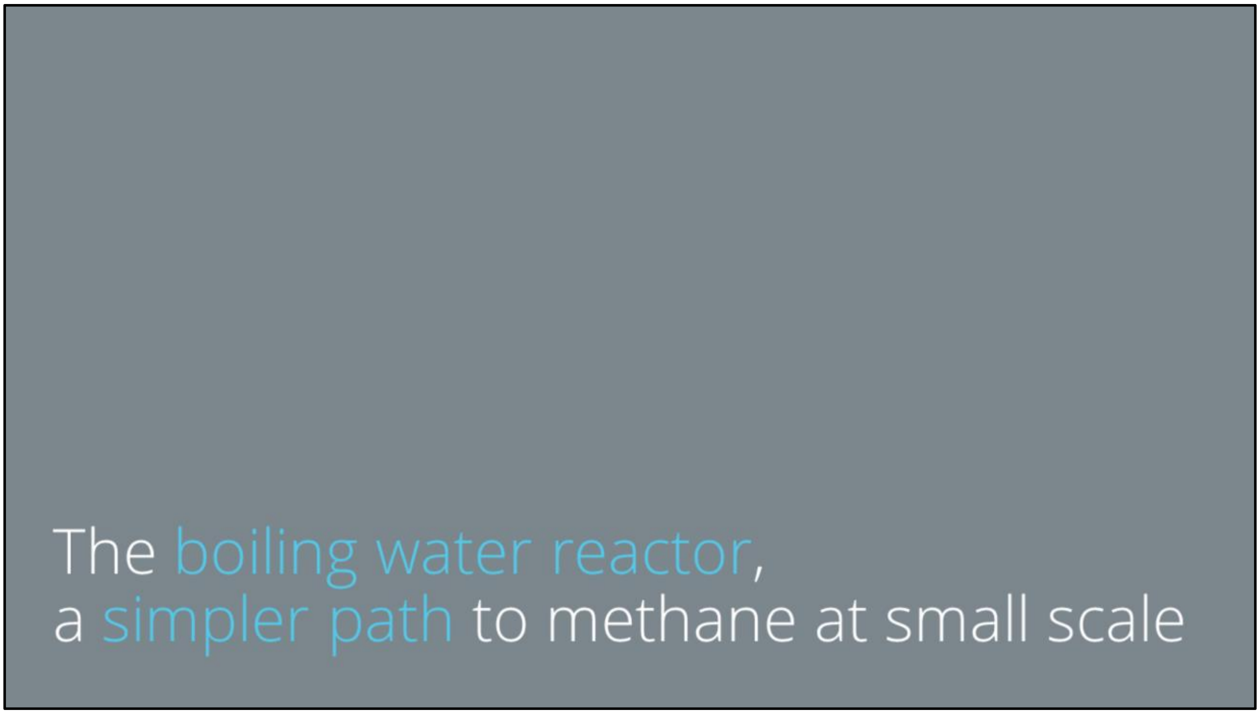
Due to the availability of wind and solar power the price for power are fluctuating. By installing a H_2 storage as a buffer the hydrogen generation can be ramped op or down in order to utilize more power when the price is low



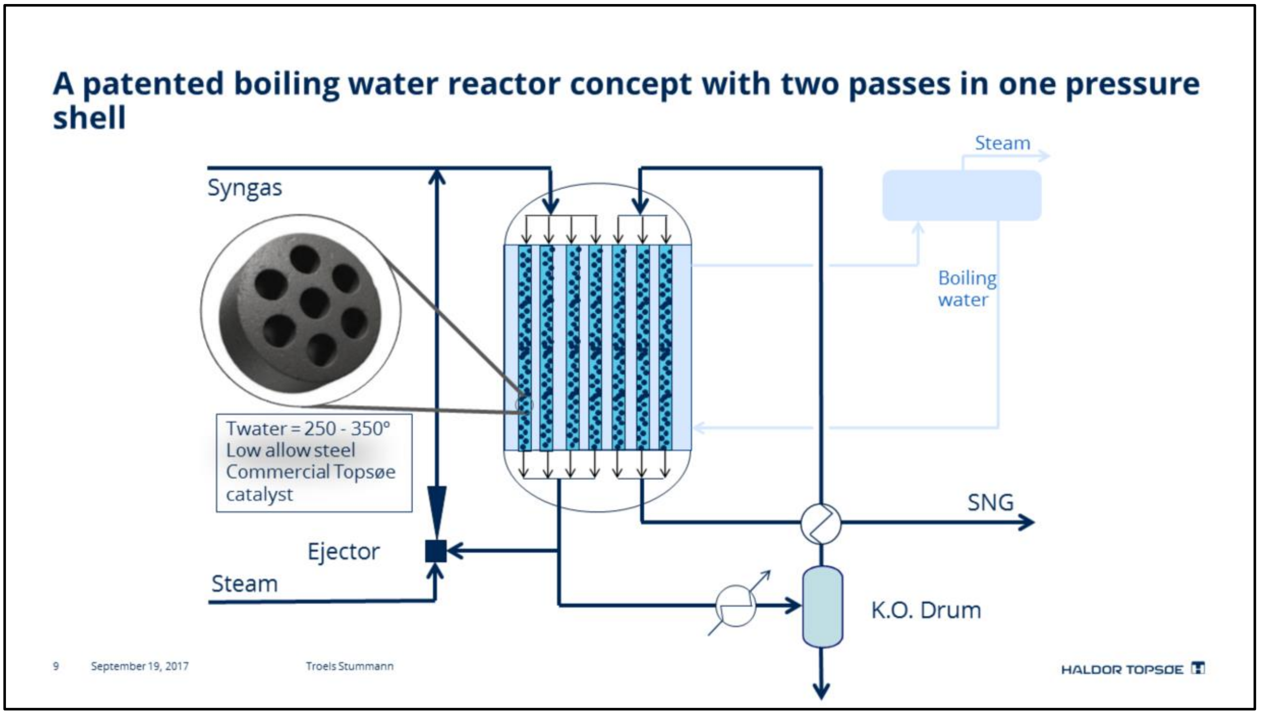
SOEC Solid oxide electrolyser cell
SOFC Solid oxide fuel cell

One option is to use SOEC which simply is a reversed SOFC
So instead of feeding syngas and produce power, then we feed power and steam and produce H_2 and O_2

SOFC have a higher efficiency than other type of electrolyses


The boiling water reactor,
a simpler path to methane at small scale

Divider



The layout with adiabatic reactors used in GoBiGas can be replaced a BWR Methanation is carried out in a multitubular reactor where the heat of reaction is transferred to boiling water.

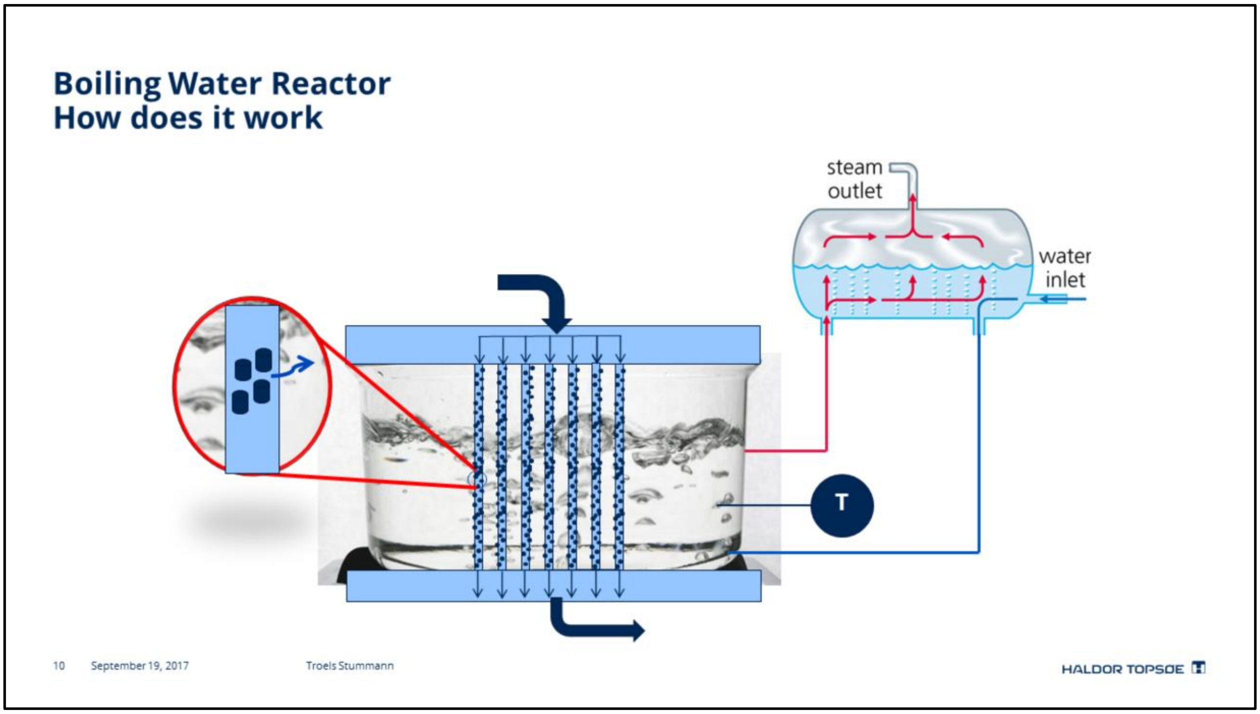
A low temperature methanation catalyst is loaded in the bottom of the tubes in order to ensure high conversion of the carbon oxides.

In the indicated layout we after reaching the equilibrium in the first pass and cooling down and knock out water then can have the 2nd pass, which is needed to reach the high conversion, in the same reactor.

In this way we replace 4-5 reactor , most of them refectory lined and a number of boilers and super heaters with one item.

This solution will for small size units reduce both CAPEX and space.

We expect that this cut the cost by about 30% compared to the adiabatic layout



The princip of the Boiling water reactor is simply that the catalyst is loaded in tubes which are submerged in boiling water.

This is a efficient way of removing heat from the process and controlling the temperature of all steel surfaces in contact with the water.

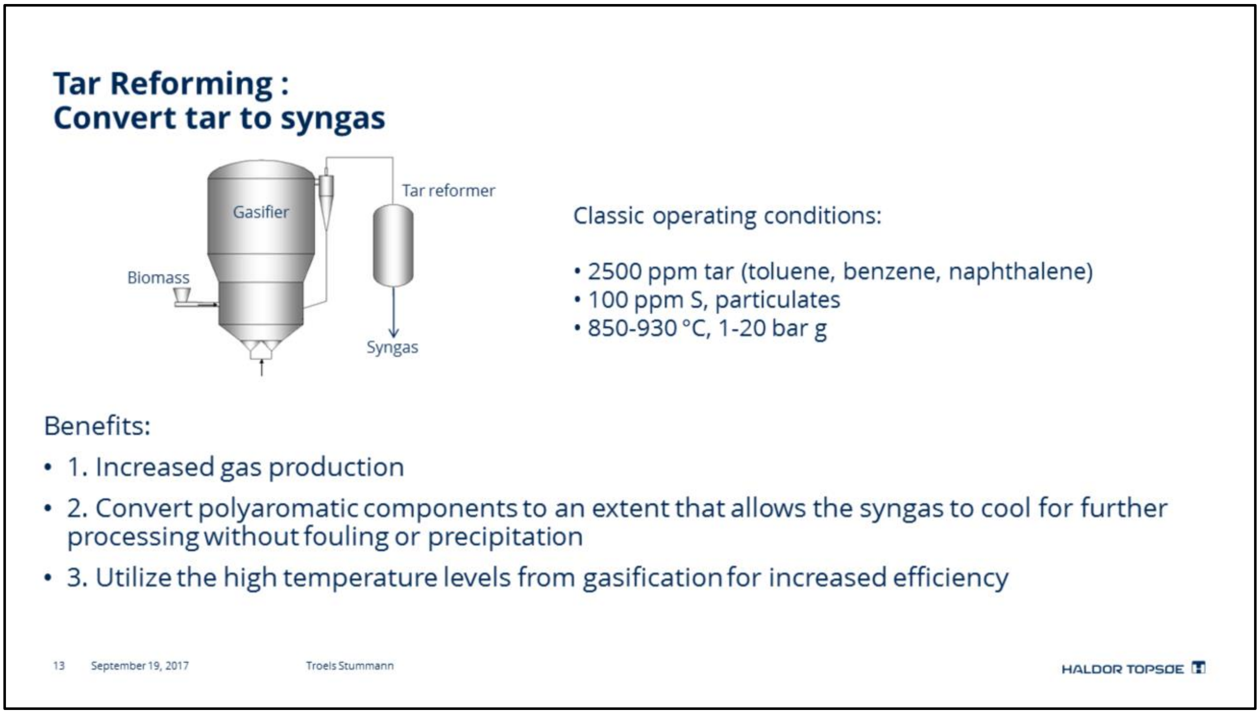
The technology comes from Topsøe methanol process and has been adapted to methanation.

We started actualy with a success full BWR pilot in Germany for SNG in 1980

Today we are mainly using the technoly for MeOH - more than 20 running MeOH BWR (14 in China)

Tar reforming

Divider



Other new features include a tar reformer.

Depending on the gasification technique, the layout consists of a catalytic tar reformer located directly downstream the gasifier's cyclone.

Tar reforming reactions

Tar hydrogenation

$C_nH_{2n} + H_2 \rightarrow nCH_4$ (exothermic)

$Tar + H_2 \rightarrow mCH_4$ (exothermic)

Methane reforming

$CH_4 + H_2O \rightleftarrows CO + 3H_2$ (endothermic)

Requires catalytic activity
- in the presence of sulfur !!

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Reactions

Steam reforming reactions, but in present of sulfur
The overall reaction is endotherm utilizing the high temperature outlet the gasifier.
Sulfur is needed to avoid carbon formation.

Have been tested at the GTI gasifier after removing the gas.
Have been in operation at a biomass gasifer in Denmark the last 5 years operating at high dust conditions
The photo show the monolith type version for high dust operation

Conclusion

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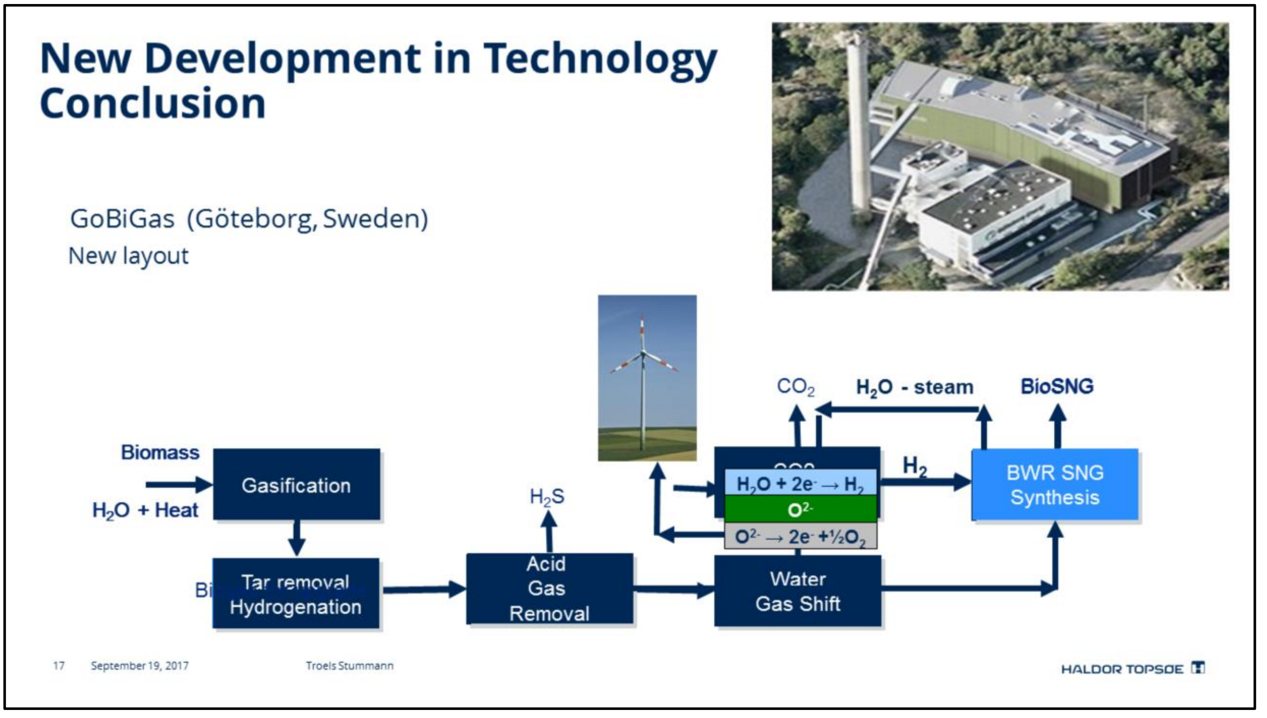


The GoBiGas layout look like this.

The new layout:

- Tar reforming replace Tar removal (and hydrogenation of Olefins)
- Acid gas Removal is still needed – but for low sulfur cases a ZnO sulfur guard migh be sufficient instead of a amine wash
- Shift section will not be needed
- CO_2 Removal are replaced with a Hydrogen generation
- The adiabatic reactors are replaced with a BWR based SNG synthesis

This approach can be used for biogas upgrading as well.

Biogas upgrade case – BioSNG Pilot, Foulum Denmark

10 Nm^3/h = 6.2 SCFM BioGas

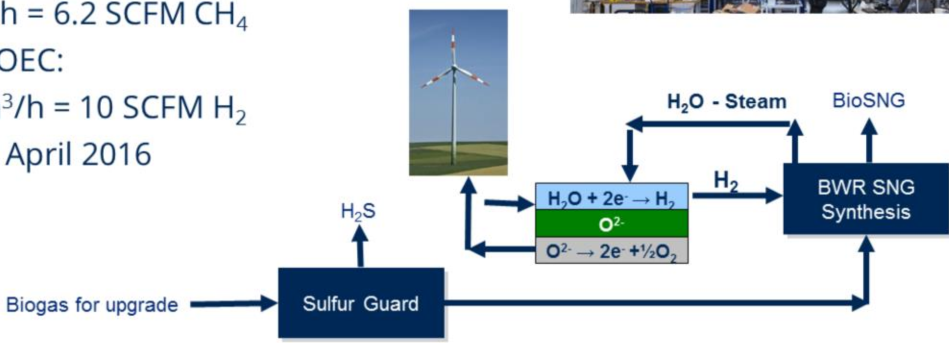
Converted to:

10 Nm^3/h = 6.2 SCFM CH_4

50 kW SOEC:

16.3 Nm^3/h = 10 SCFM H_2

Start-up April 2016



This unit was set in operation in april 2016 in Denmark for upgrating Biogas from biomass fermentation to SNG

BioSNG Pilot, Foulum Denmark
Gas compositions for biogas upgrade

	CH_4	CO_2	N_2	H_2
Inlet	56	43	1	0
Product gas	97.69	0.00	0.95	1.36

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This is data from the plant: the Biogas have successful been upgraded from 56 mol% to more than 97 mole % Methane


Thank You
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