Advanced Green Gas Technology

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Energy Delta Gas Research

ECN
Your energy. Our passion.

Advanced Green Gas Technology

Luc Rabou
Amsterdam, March 19, 2015

university of groningen
Delft University of Technology
Hanzehogeschool Groningen University of Applied Sciences

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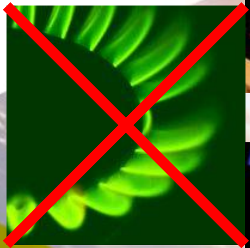

university of groningen
gasunie
DNV·GL
TU Delft Delft University of Technology
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Motivation

- Gas is and will be an essential part of our energy supply
- Reduction of CO_2 emissions requires renewable substitute (bio-SNG)
- Cost and availability of biomass make it essential to develop efficient & versatile conversion technology

AGATE 1 + 2 & Synthetic Methane

- ECN — L. Rabou, E. van Dijk, W. Haije, M. Saric, J. Dijkstra
  Dry biomass gasification => CH_4
  $H_2 + CO_2$ (+ ……)=> CH_4
- RUG ST/OC — H. Heeres, A. Kumalaputri, V. Hornillos, A. Phua
  Wet biomass gasification => CH_4
- RUG CIO — S. Palstra, H. Meijer
  ^{14}C analysis for "green" gas
- DNV GL — H. Roeterink — **Cost price and gas quality**
- Hanze — M. Barankin — **LCA P2G, µCHP**
- TUD — P. Aravind — **Solid oxide fuel cell/electrolyser**

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CH_4 production from dry biomass

1. Gasification: conversion of solid biomass to producer gas
2. Producer gas cleaning: removal of dust, tar, catalyst poisons
3. Producer gas conversion to CH_4, CO_2 and H_2O
4. Upgrading to gas grid specifications

ESME: **E**CN **S**ystem for **Me**thanation

Gasification

Lab-MILENA

DAHLMAN

Quick biomass heating to 750 – 850 °C

⇒Producer gas CO, H_2, CO_2, CH_4, C_xH_y, H_2O, N_2
+ NH_3, HCN, C_xH_yN
+ H_2S, COS, C_xH_yS
+ dust + Cl-compounds

⇒Char carbon-rich residue

- Char combustion provides heat for process
- Gas cooling can be used for steam/E production

Low or high temperature gasification

MILENA gas

Component	*Vol % (dry)*	*Energy %*	*Efficiency‡ %*
$CO + H_2$	60	40	77
CH_4	13	27	100
C_2H_2	0.3	1	81
C_2H_4	4.2	14	89
C_2H_6	0.3	1	96
C_3H_6	0.1	0.5	90
C_6H_6	1.0	8	90
C_7H_8	0.1	1	91
Tar	0.3	6	91
$CO_2 + N_2$	20		

‡ heating value

$X + H_2 \Rightarrow CH_4$

$C_2H_2 + C_2H_4 + C_3H_6$
$+ C_6H_6 + C_7H_8$

≡

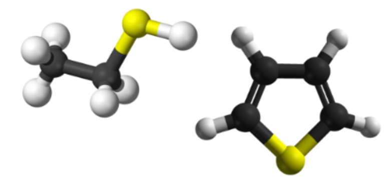
± 25% of producer gas heating value

Gas cleaning

Dust and tar removal OLGA

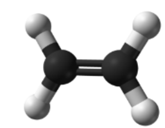
(tar = aromatic hydrocarbons, heavier than benzene)

Removal of catalyst poisons

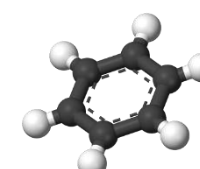


focus on organic sulfur compounds

Hydrogenation of unsaturated hydrocarbons



(Pre)reforming of aromatic hydrocarbons (BTX)



Catalytic gas cleaning (1)

Lab-HDS

Hydro De Sulfurization (HDS) catalyst

- Opens ring structure containing S atom

  => produces H_2S or COS (to be removed) →

- Breaks down organic N compounds,

  including HCN, but not NH_3

- Adds H_2 to unsaturated hydrocarbons

  => produces e.g. C_2H_6, C_3H_8

Lab-reactors with adsorbents (AGATE 2)

HDS test rig built and operating conditions optimized in AGATE 1

Catalytic gas cleaning (2)


Lab reforming + methanation

Pre-reforming catalyst

- Converts aromatic hydrocarbons (BTX) with steam into CO and H_2 — Requires heat
- Acts also as methanation catalyst — Produces heat

Prone to carbon deposition

Critical for system performance (degradation)

Test rig built and operating conditions optimized in AGATE 2

Methane production (nickel catalyst)

Main methanation reaction: $CO + 3H_2 \Leftrightarrow CH_4 + H_2O$ (+ heat)

Equilibrium shifts to CH_4 at high pressure and low temperature

Other reactions: $C_2H_6 + H_2 \Rightarrow 2\ CH_4$ (+ heat)

$C_3H_8 + 2\ H_2 \Rightarrow 3\ CH_4$ (+ heat)

H_2 shortage calls for water gas shift: $CO + H_2O \Leftrightarrow CO_2 + H_2$ (+ heat)

or H_2 from another source (P2G)

Upgrading

Final product consists of CH_4, CO_2, H_2O and some H_2 (+ some N_2 and NH_3)

$\Rightarrow$ CO_2 and H_2O removal (at 5 – 10 bar)

Yields CH_4 with 5% H_2, 3-5% N_2, and < 0.03% CO

$\Rightarrow$ Further compression and final methanation (at 30 – 40 bar)

or H_2 separation / acceptation

CO_2 removal or P2G?

$CO_2 + 4\ H_2 \Leftrightarrow CH_4 + 2\ H_2O$ (+ heat) Sabatier reaction

Can be applied to pure CO_2, biogas or producer gas

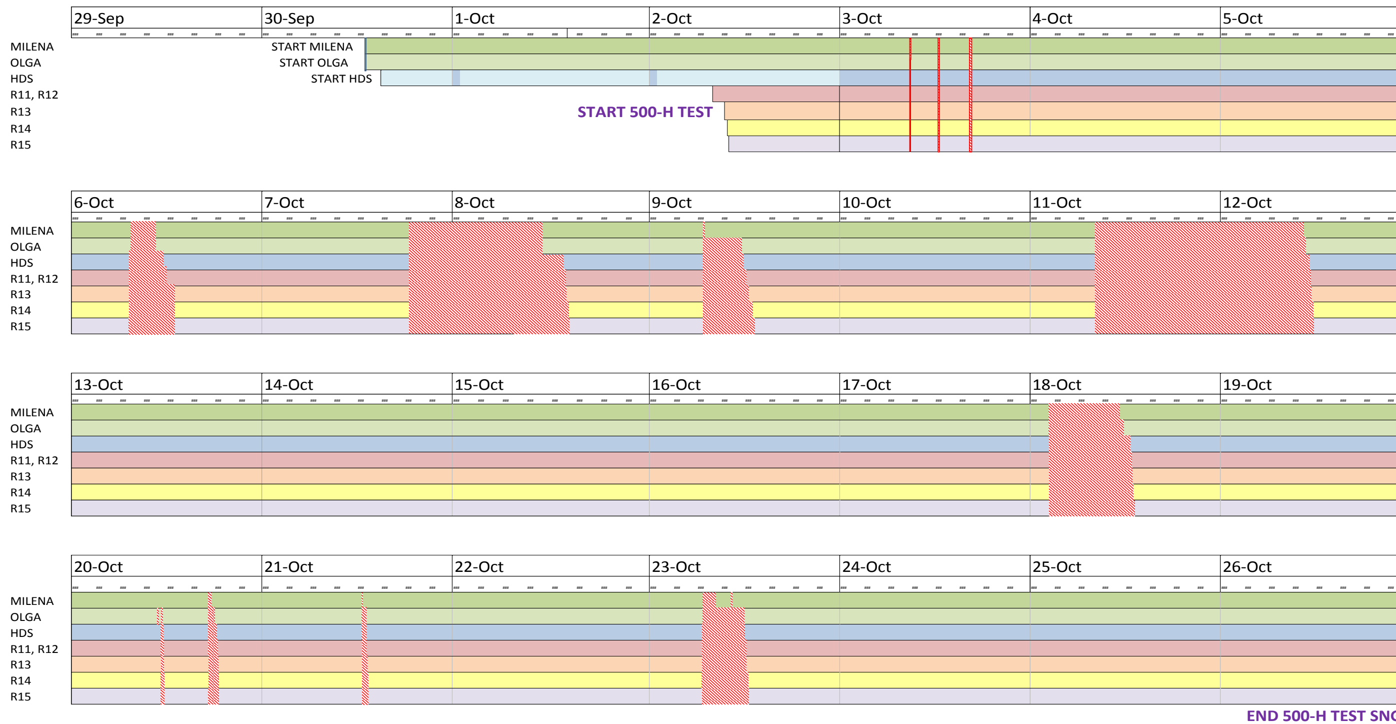
- Could double CH_4 production in case of biogas and producer gas
- Saves effort for CO_2 removal
- Requires 30 – 40 bar pressure for low final H_2 content
- Changes system heat management

System analysis, test rig modification and exploratory experiments
in Synthetic Methane

500 hrs ESME performance test

Wood gasification, gas cleaning and 6 bar methanation

~1 m^3/hr producer gas (~3 kW)



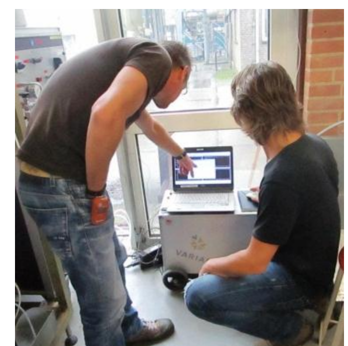
Thanks to team



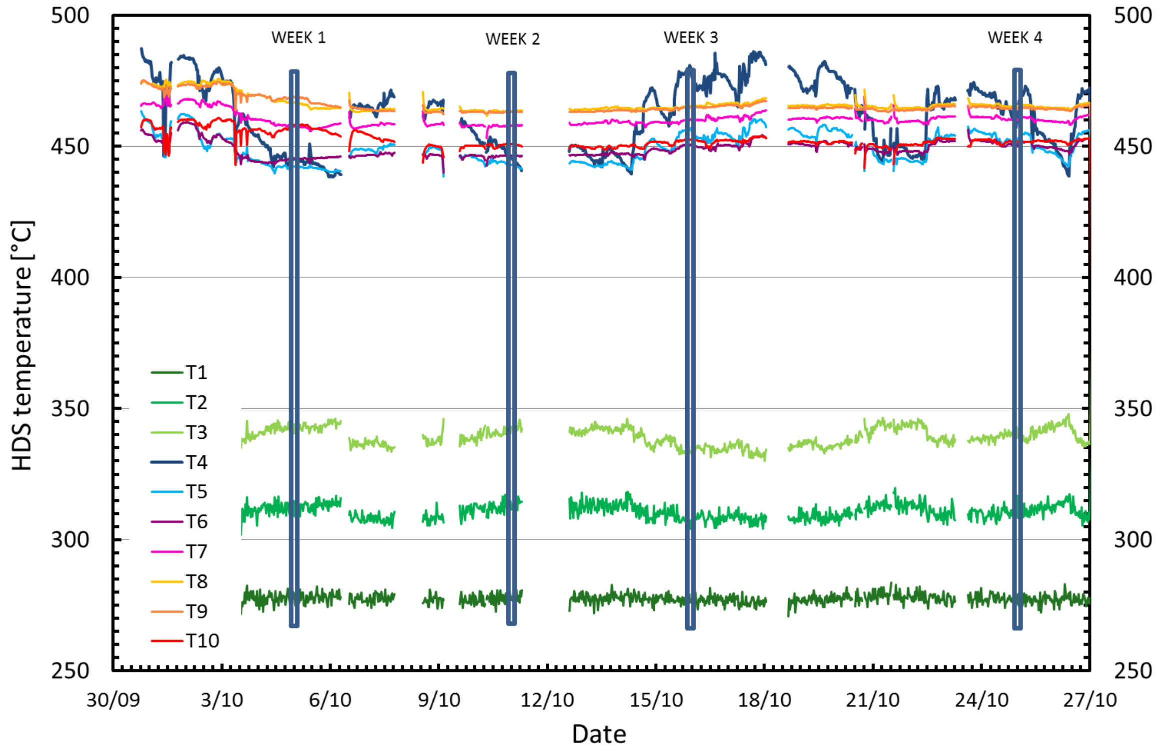


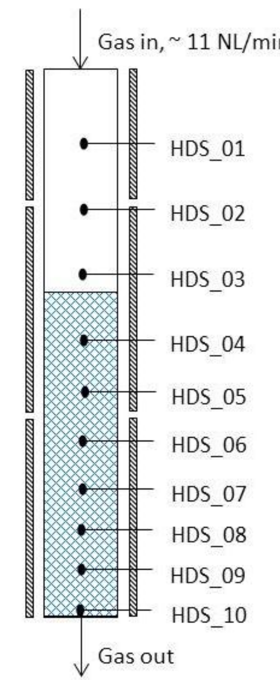




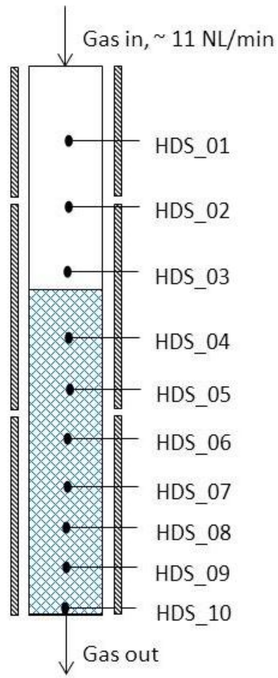



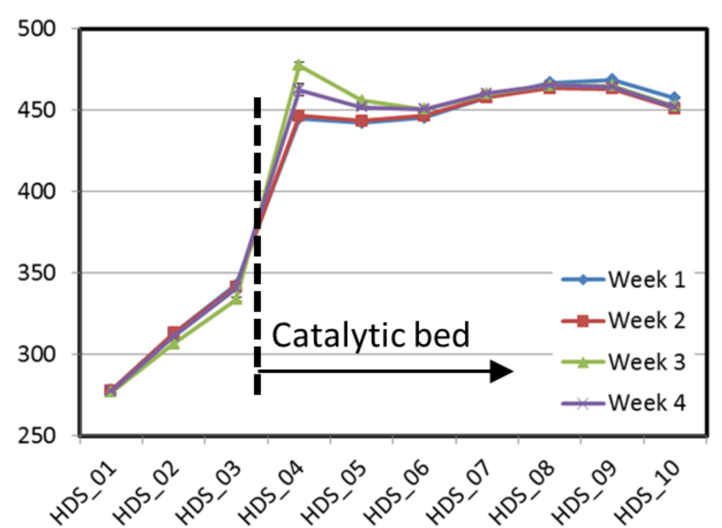

HDS temperatures





HDS temperature profile





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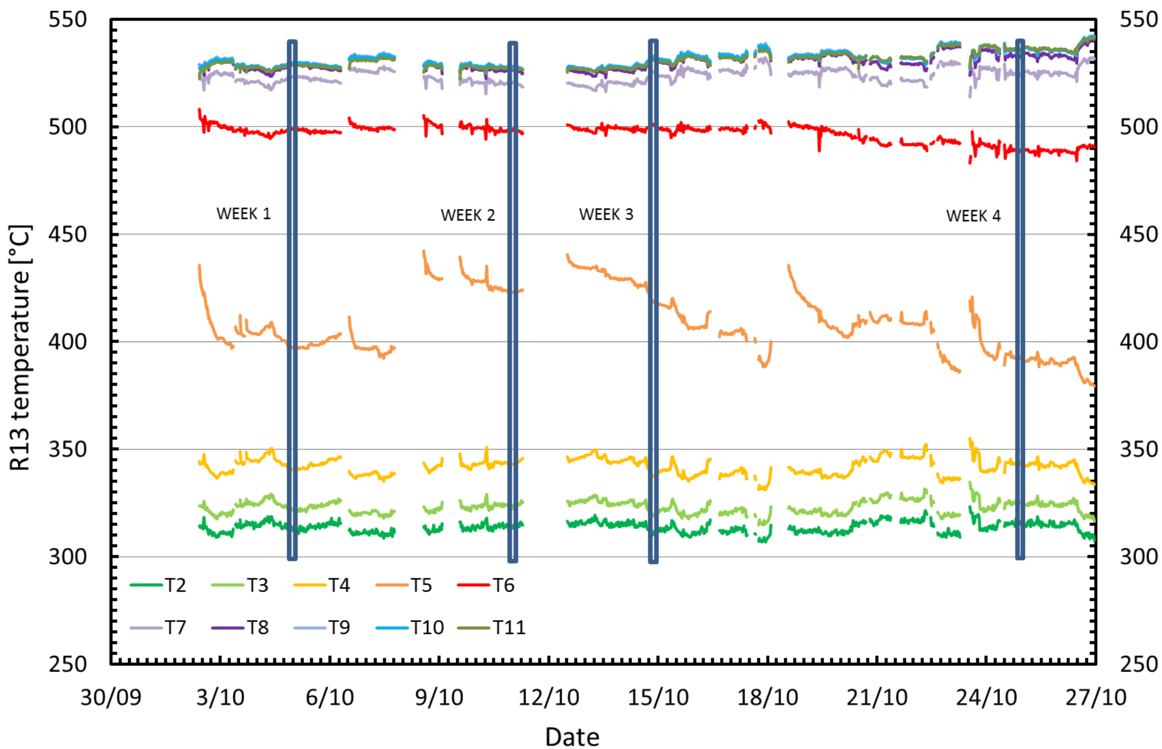
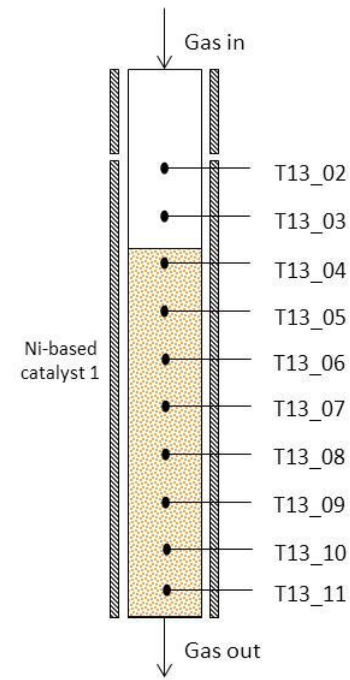
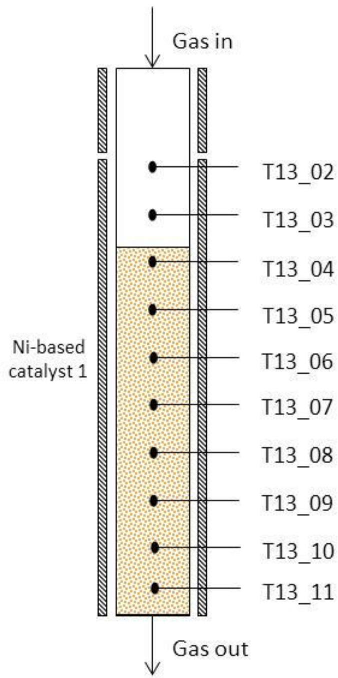
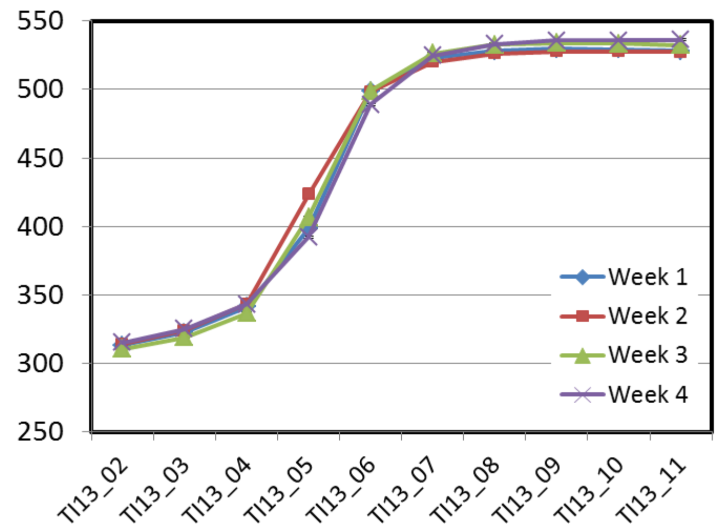
Prereformer temperatures



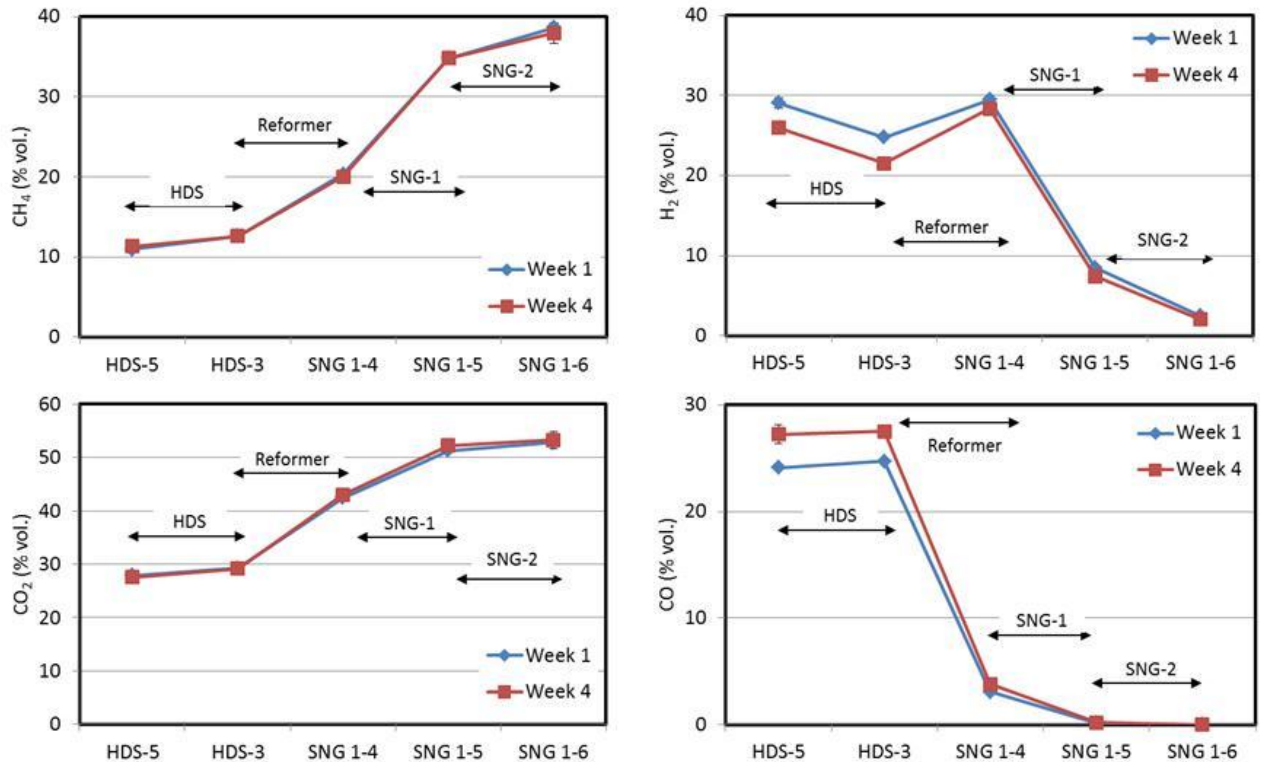


Prereformer temperature profile





Gas composition



Summary of 500 hrs test

- Temperature profiles show no indication of catalyst degradation

  Commercial operation requires >20 times longer

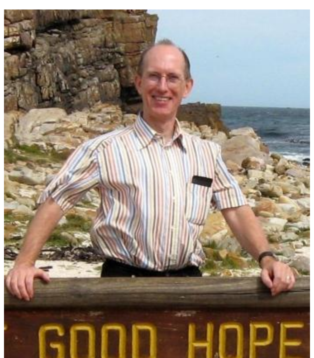
- Final gas composition stable
- Residual CO ~130 ppm (< 300 ppm after CO_2 removal)
- Residual H_2 ~2% (< 5% after CO_2 removal)

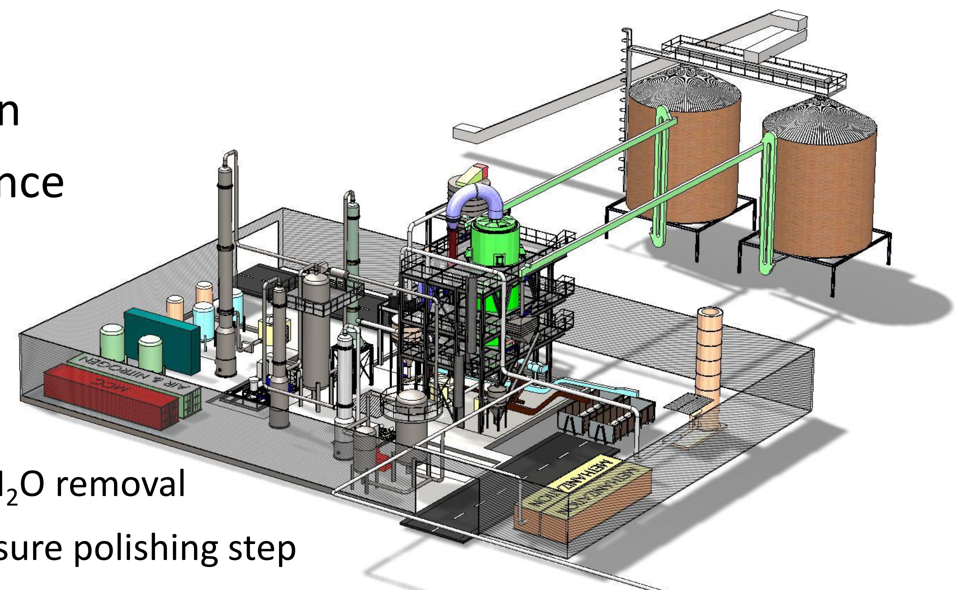
- **Important step for scale-up of bio-SNG production**

  → 300 m^3/h SNG facility to be built in the Netherlands

Conclusion

- Test equipment available for gas cleaning, methanation and P2G tests
- Sulfur removal to 0.1 ppm proven
- BTX (pre)reforming successful
- ESME design for bio-SNG production
- 500 hrs test shows stable performance
- Bio-SNG consortium for 4 MW system





  - Includes CO_2 and H_2O removal
  - Includes high-pressure polishing step
  - Aims at > 5000 hrs/year

Thanks to EDGaR sponsors

Investing in your future

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Be prepared to pay more

Current wholesale prices (approximately)

• Natural gas		0.22 €/m^3	7 €/GJ	25 €/MWh
• Electricity			11 €/GJ	40 €/MWh
• Wood	50 €/ton		5 €/GJ	18 €/MWh

• Electricity → H_2	> 15% loss	> 13 €/GJ	+ electrolyser
• Electricity → H_2 → CH_4	> 25% loss	> 15 €/GJ	+ electrolyser + methanation
• Wood → → CH_4	> 30% loss	> 7 €/GJ	+ gasification + gas cleaning + methanation + CO_2 removal

=> Optimize efficiency and reduce costs

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