SNG quality in Power to Gas applications

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EDGaR - 6th Research day
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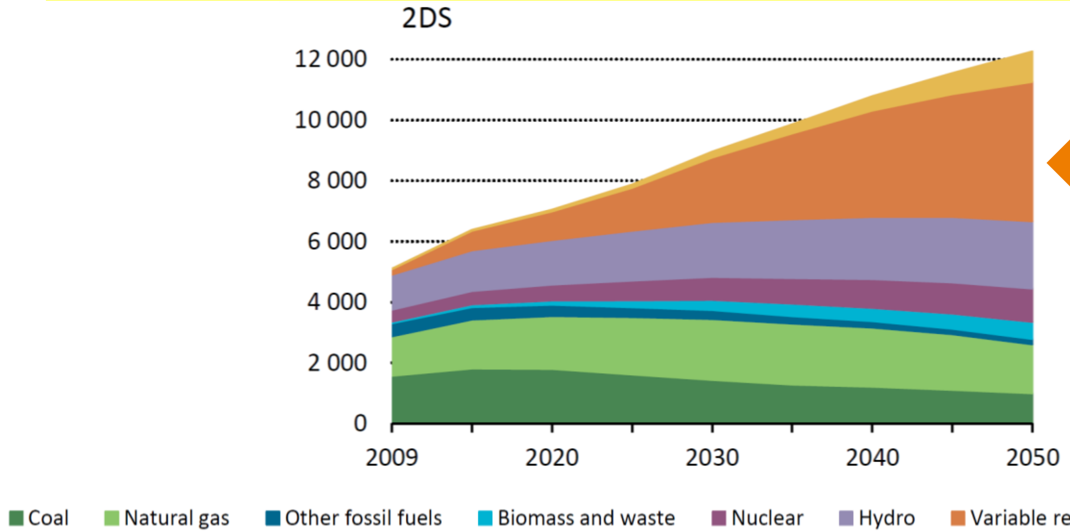
The Netherlands

The future global electricity mix



Increasing share of variable renewables

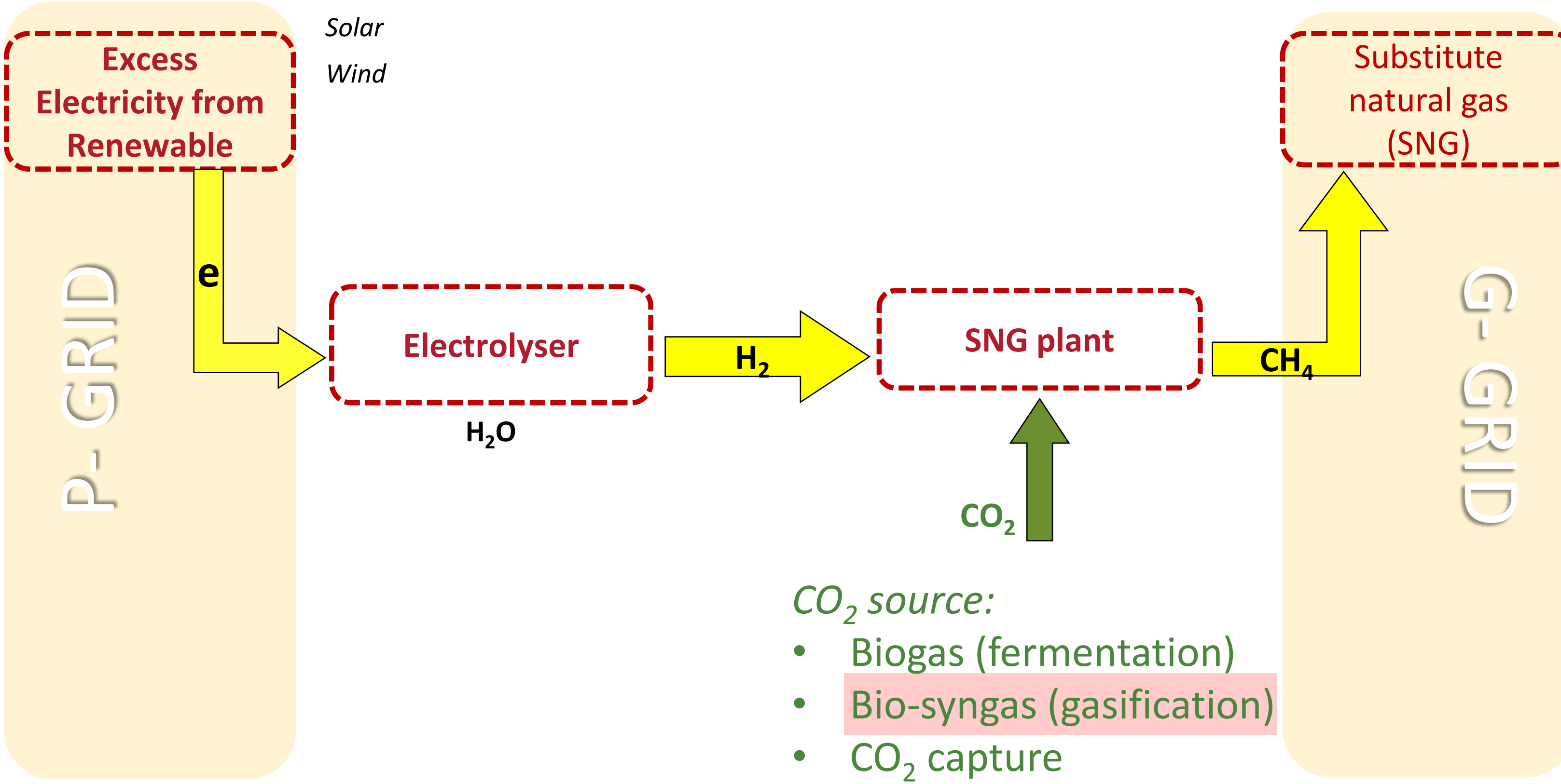
Source: IEA ETP, 2012

➔ Not all green power can be fed into the electricity grid due to:

- Mismatch in time
- Mismatch in location (transport limitations)

} Excess renewable electricity

Power-to-(Green)-Gas



CO_2 source:

- Biogas (fermentation)
- Bio-syngas (gasification)
- CO_2 capture

$$CO_2 + 4\,H_2 \Leftrightarrow CH_4 + 2\,H_2O$$

EDGAR Synthetic methane project

SOE, Solid Oxide Electrolyzer (TUD)

- Characterization, modeling and development

Focus →

Methanation (ECN)

- Feedstock & product quality
- Gas cleaning
- Unit operation development
- Process design

Integration and market aspects (Hanze, ECN, TUD)

- Preferred configurations
- LCA & chain efficiency
- Market opportunities

TU Delft Delft University of Technology

ECN

Hanze University Groningen University of Applied Sciences

Objectives

Process

1. Configurations and conditions
2. Flexibility impact

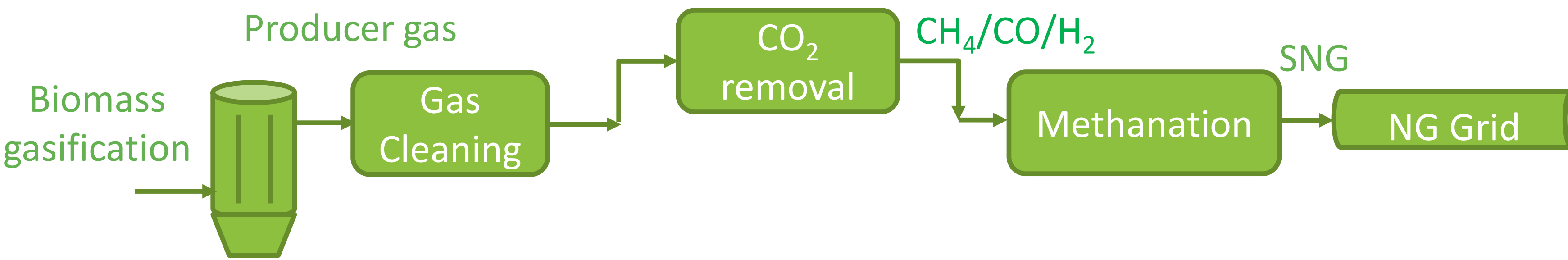
Gas quality

1. Thermodynamic assessment
2. Experimental
3. Novel process

Take home messages

- Power-to-gas for producer gas upgrade can almost double SNG production
- Low impact on SNG quality, H_2 limit in the grid point of attention
- Successful experimental results with methanation, equilibrium obtained
- "Proof of principle" with novel sorption enhanced (SE)-methanation, close to 100% conversion

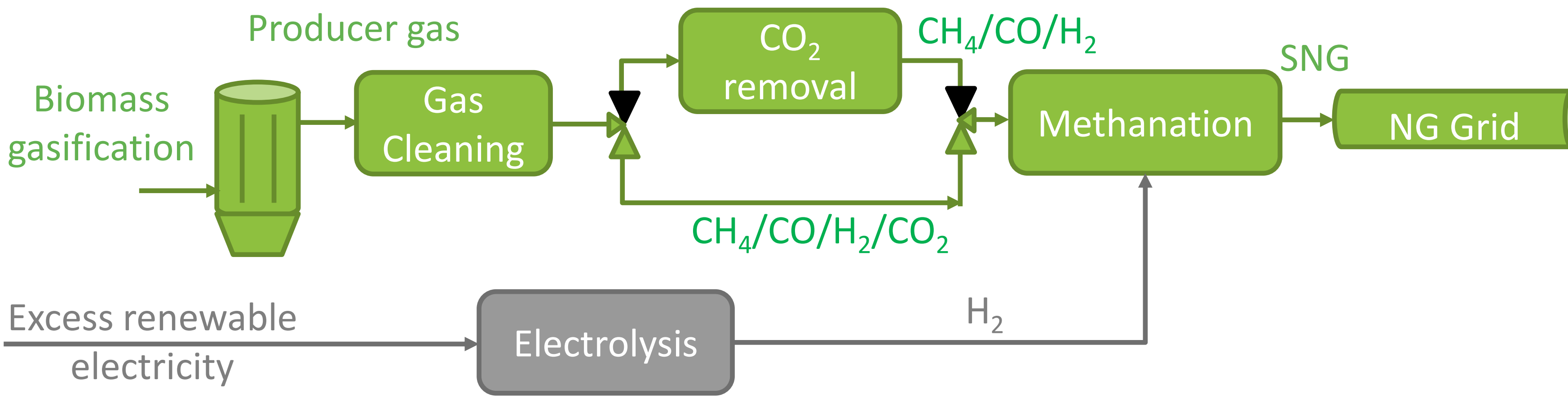
Systems modes evaluated: *E-demand*



Stream composition after gas cleaning:

Mole Frac	
H2	38.78%
CO	8.57%
CO2	32.48%
CH4	18.52%

Systems modes evaluated: *E-excess*



Stream composition after gas cleaning:

Mole Frac	
H2	38.78%
CO	8.57%
CO2	32.48%
CH4	18.52%

➔ Switch between two modes

System starting points

ECN biomass gasification technology

- MILENA indirect gasifier
- OLGA tar removal

SOE electrolyzer

- Pure H_2 available a at required pressure

Gas cleaning

- Water scrubbing
- COS/H_2S removal
- Pre-reforming
- Pre-compression

CO_2 removal (MEA) [with bypass]

Methanation

SNG upgrade

- Water removal
- Compression to grid pressure [60 bar]

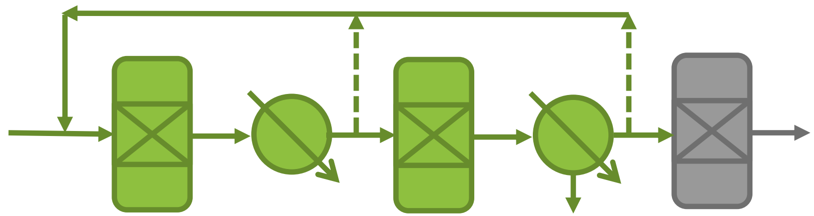
Battery limits

800 kW MILENA pilot gasifier

Design variables

Methanation configuration:

multi-stage process with 3 intercooled fixed bed reactors



Presented here

- Configuration 1: high temperature T_{max}=650°C, 3 stage, recycle after 1st stage } Lurgi HT
- Configuration 2: high temperature T_{max}=650°C, 3 stage, recycle after 2nd stage } Great Plains
- Configuration 3: low temperature T_{max}=450°C, 2-stage recycle after 1st stage

Methanation section pressure

- 20-60 bar

Criteria

Wobbe index

$$W = \frac{HHV}{\sqrt{(\rho_g / \rho_{air})}}$$

W> 43.5 MJ/Nm^3 Dutch gas grid standard

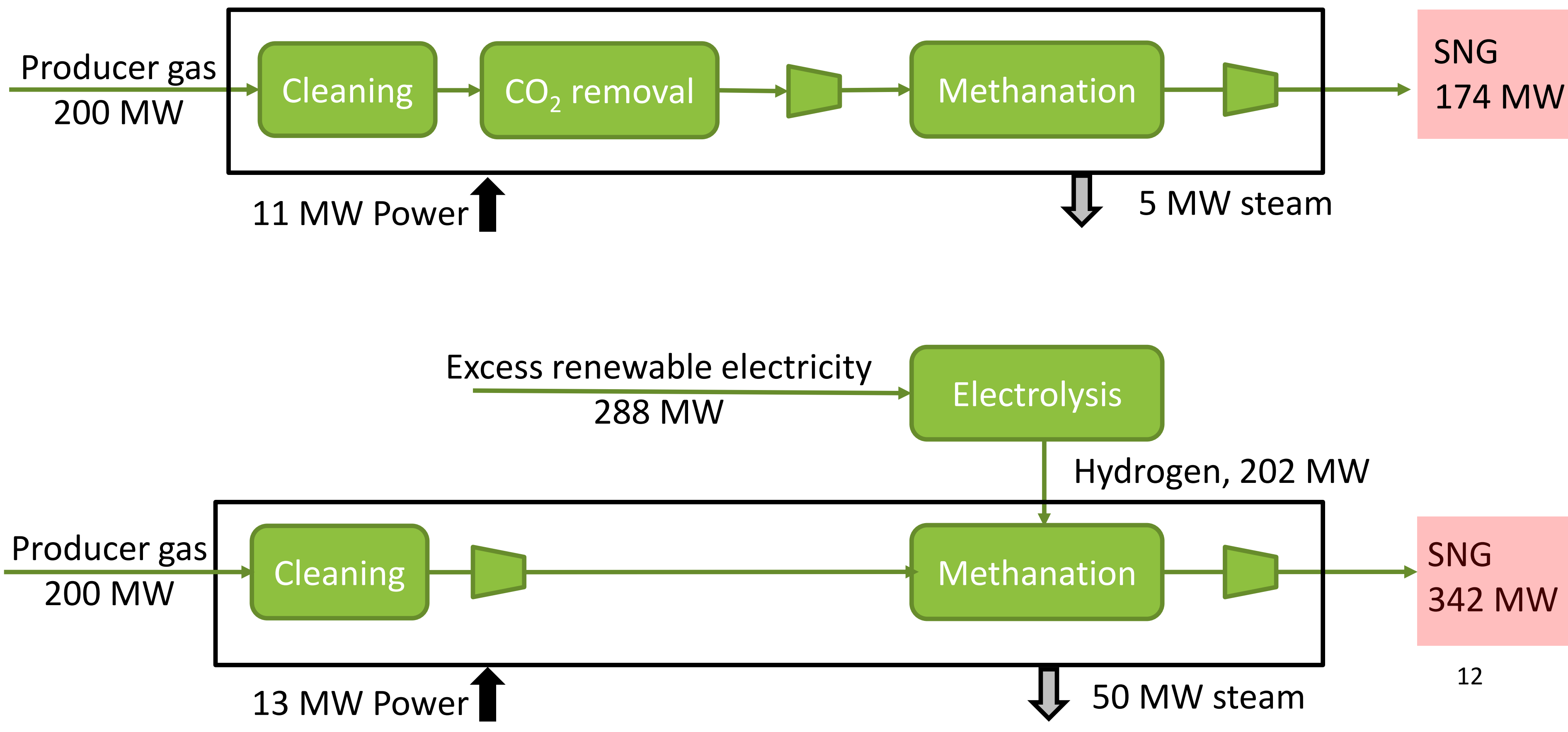
SNG molar H_2 Content

- *Max1*<0.5% H_2 — Dutch gas grid standard
- *Max2*< 10% H_2 — Possible future limit

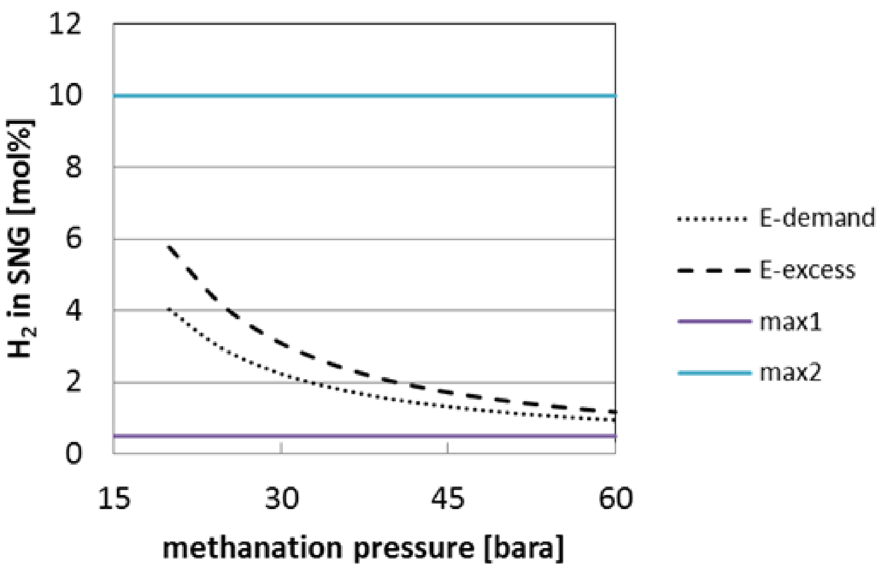
Energy balance

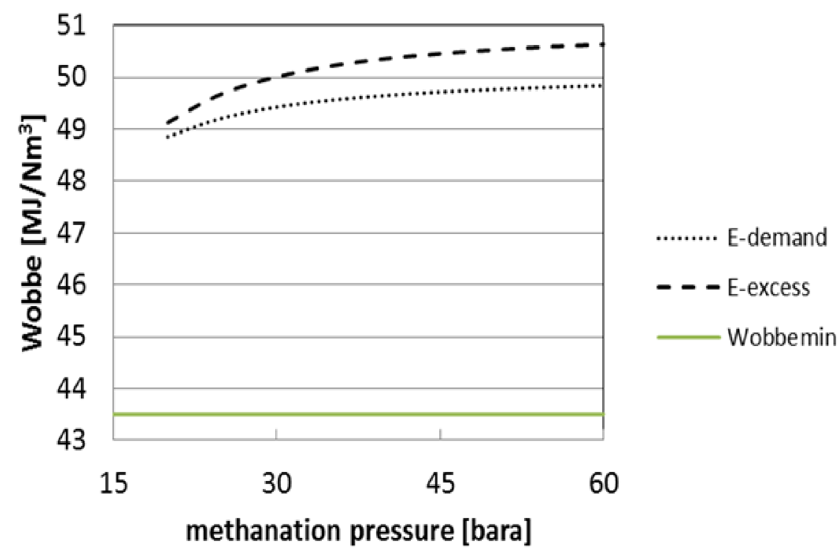
- Steam balance
- Total power use

Comparison: *E-demand* vs. *E-excess*



Gas quality: *E-demand* and *E-excess*



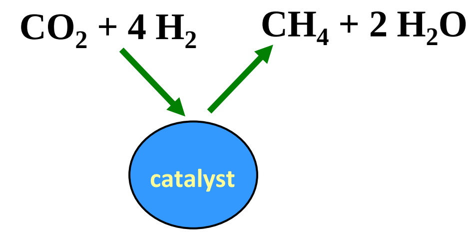


H_2 addition in *E-excess* has low impact on the gas quality

Sorption Enhanced (SE-)Methanation

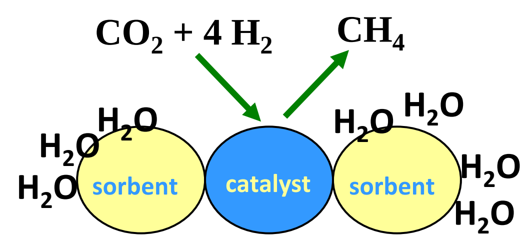
CO_2 Methanation reaction

$CO_2 + 4\ H_2 \Leftrightarrow CH_4 + 2\ H_2O$



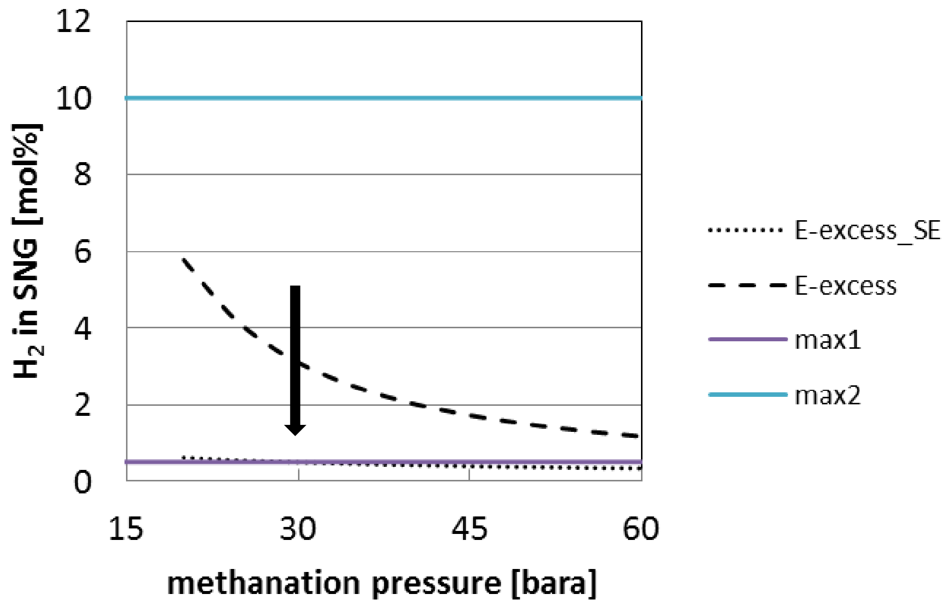
CO_2 Methanation reaction + Water removal

$CO_2 + 4\ H_2 \Leftrightarrow CH_4 + 2\ H_2O$



Enhanced reactants conversion

Gas quality: SE-methanation



Assumptions:

- 2 conventional reactors
- 3rd reactor SE-methanation
- T= 250°C
- Water removal is 90%

➔ H_2 level target of *Max1* met at operating pressures of 30 bar

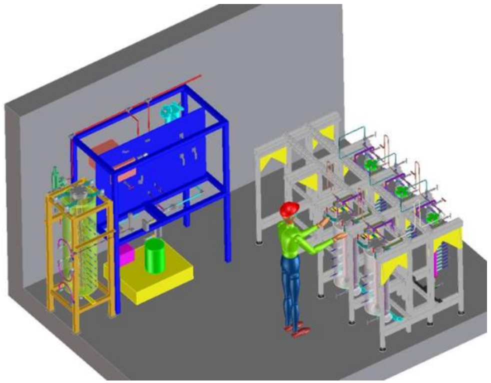
Conclusions & Outlook
System studies

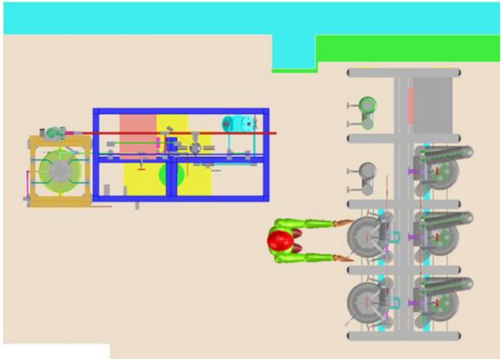
- Power-to-gas is a flexible solution that can double the SNG production
- Switch between *E-demand/E-excess* has limited impact on SNG quality
- H_2 amount is point of attention
- SE-methanation is a possible solution to obtain allowable H_2 contents

Outlook

- Other feedstocks
- Sour methanation

Test facility for methanation





HDS + SNG

- Methanation: 3-reactor in series test-rig
- Operating with real producer gas
- Pressurized system, 6 bar

ECN

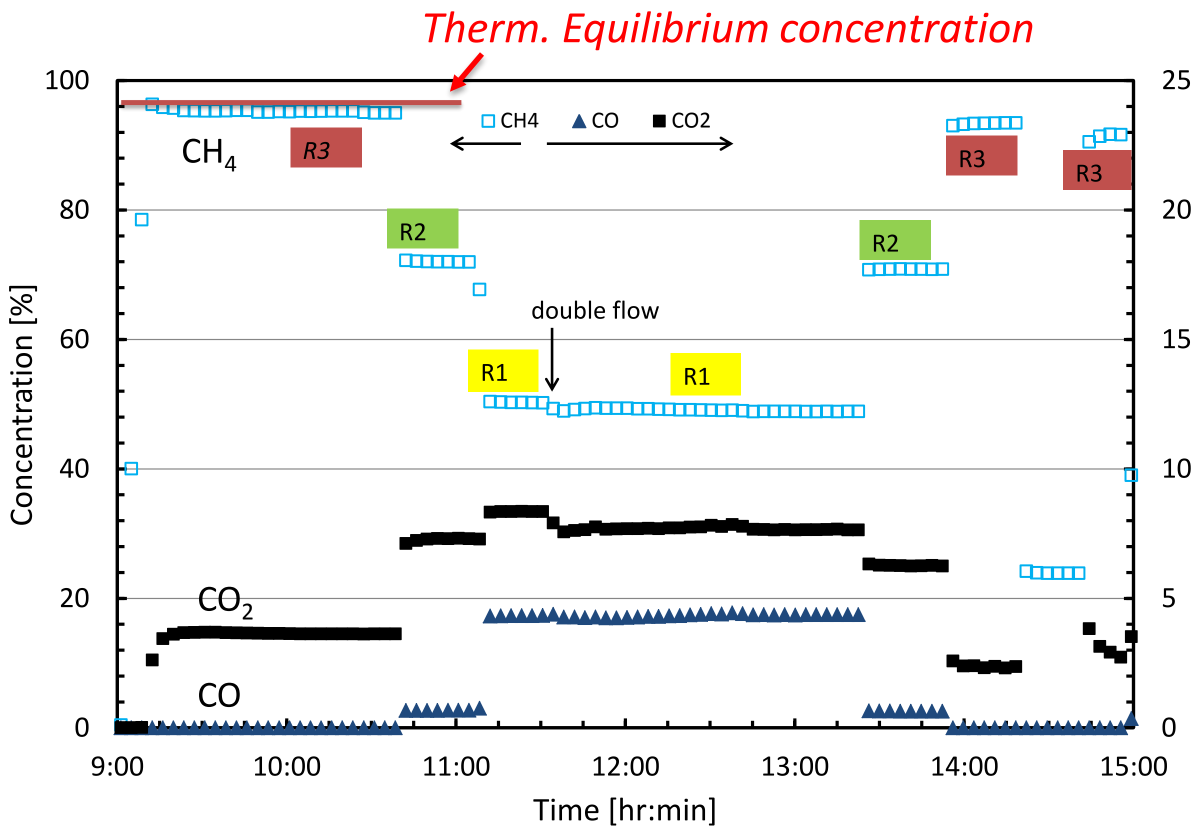
Biogas methanation

Goal : Experimental verification biomass to SNG with commercial Ni-based catalyst, not designed for CO_2 feed

Simulated biogas	mol%
H_2	61.6%
CO_2	14.7%
CH_4	22%
Ar	1.7%

- T_{inlet}~ 250°C , p= 6 bara, GHSV = 1,000 -2,000 h^{-1} , tests w/wo steam addition

Results – biogas methanation

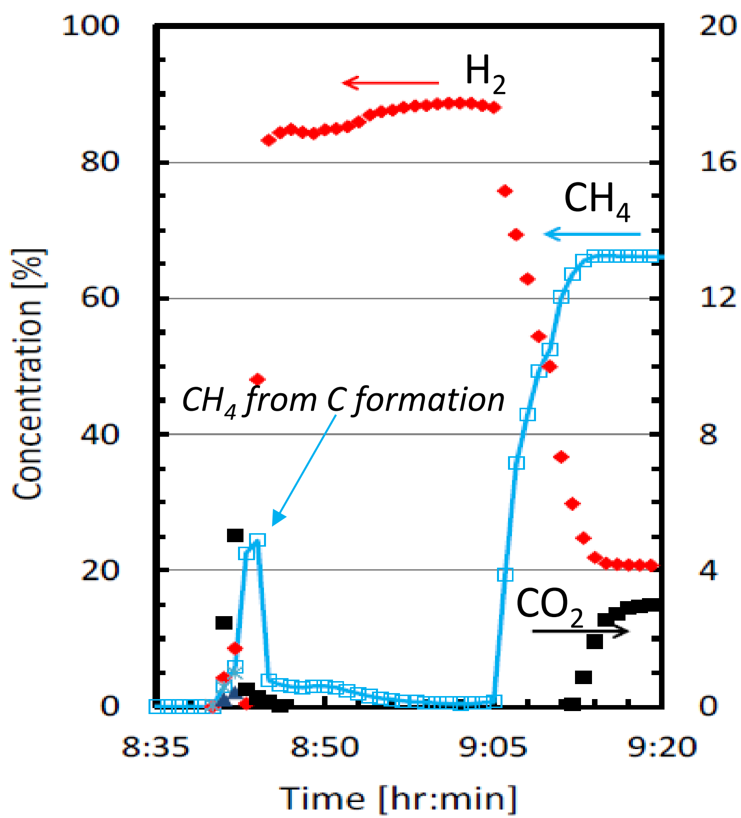


In: 5% excess H_2 to 60/40 CH_4/CO_2

Conversion in 3 adiabatic reactors (R1, R2, R3) with 250°C inlet temperature

Out: equilibrium at reactor temperatures (600°C, 480°C and 350°C)

Results –biogas methanation



Post-test analysis of catalyst in 1st reactor.

Feeding pure H_2 to catalyst at 250°C.

CH_4 formation during H_2 addition indicates that some coke formation has taken place during the previous methanation experiments.

Conclusions & outlook biogas methanation

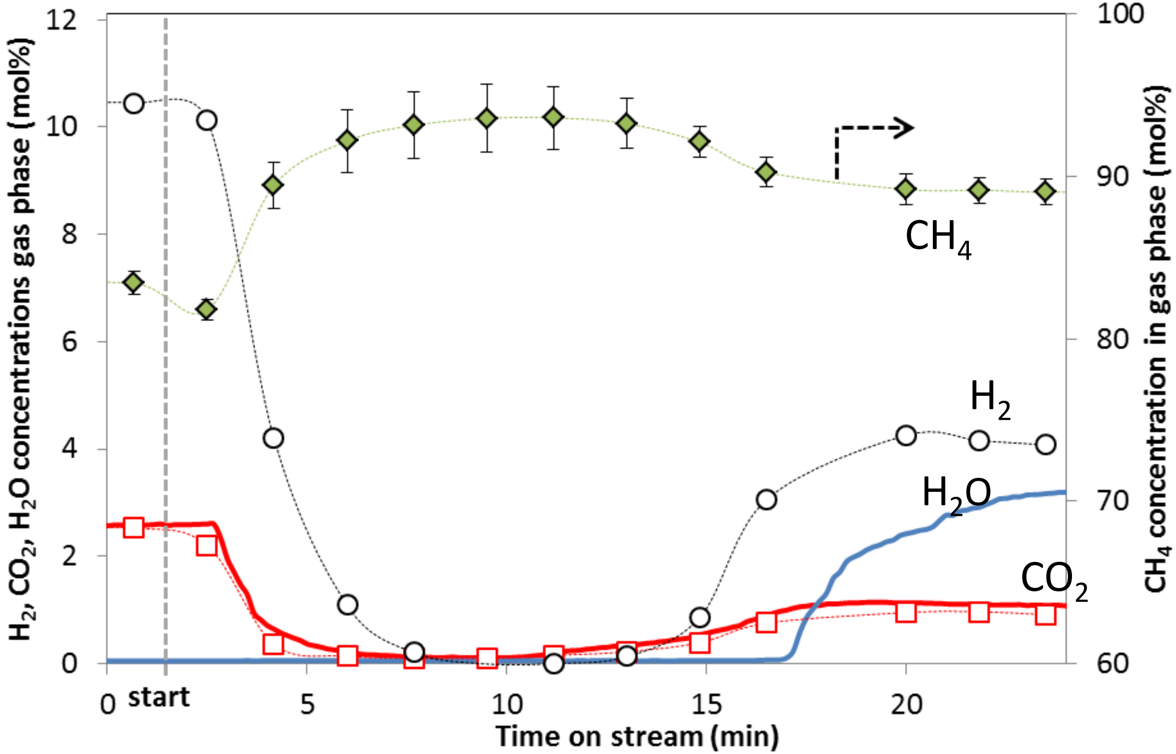
ECN

- Successful tests with biogas mixture with commercial catalyst (Thermodynamic conversion reached)
- Doubling of flow (at low GHSV) does not have influence on conversion
- Carbon formation observed in the first reactor

Outlook

- Tests with bio-syngas planned
- Address carbon formation

Experimental results SE methanation



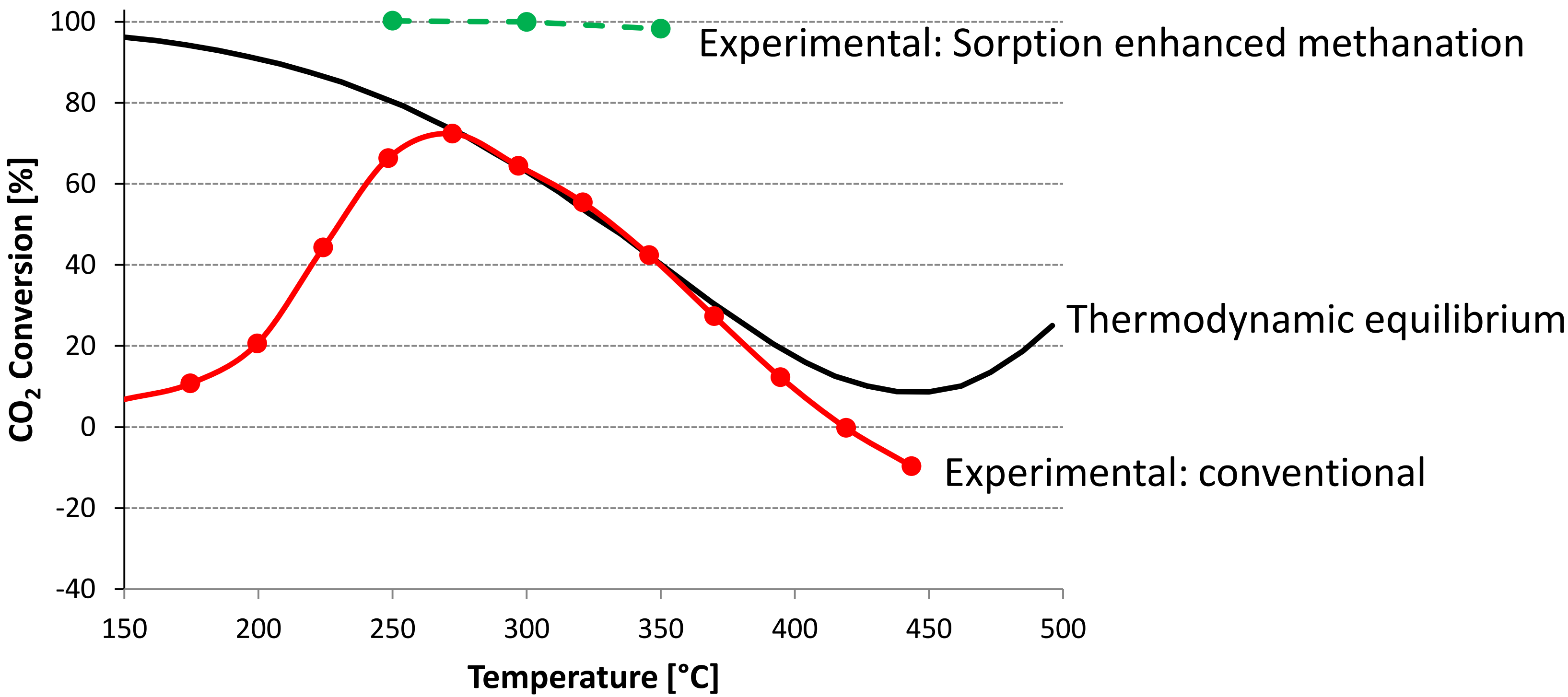
Inlet composition:
2.5% CO_2, 9.9% H_2, 81.6%CH_4, and 6%N_2
P = 1 atm, total flow = 150 ml/min,
T=250°C, 3.6 g (Zeolite 4A:cat=5:1)
Regeneration: N_2 and H_2

- No H_2O in product gas due to adsorption on zeolite
- No H_2, CO_2 in product gas due to SE methanation
- Break-trough after 13 minutes

Commercial Ni-based cat + Zeolite 4A

*S.Walspurger et al., Chemical Engineering Journal 242 (2014) 379-386

Experimental results
CO2 conversion



Inlet composition: 2.4% CO_2, 9.4% H_2, 77.8%CH_4,4.7%H_2O and 5.6%N_2
P = 1 atm, total flow = 150 ml/min, 3.6 g (alumina/cat = 5:1), GHSV=2500 h^{-1}

Conclusions and outlook– SE methanation

- Proof-of-principle with commercial catalyst + sorbent

Outlook

- Optimization of adsorbent/catalyst materials
- Regeneration options

Conclusions

- Power to gas for bio-syngas upgrade can double SNG production with low impact on SNG quality

- H_2 limit in the grid is point of attention

- Successful experimental results with biogas methanation, equilibrium obtained

- “Proof of principle” with novel sorption enhanced (SE)-methanation, close to 100% conversion

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