Potential of “Power to Gas” conversion chain integration with Biomethane Production

M. Sarić
J.W. Dijkstra
S. Walspurger
W.G. Haije

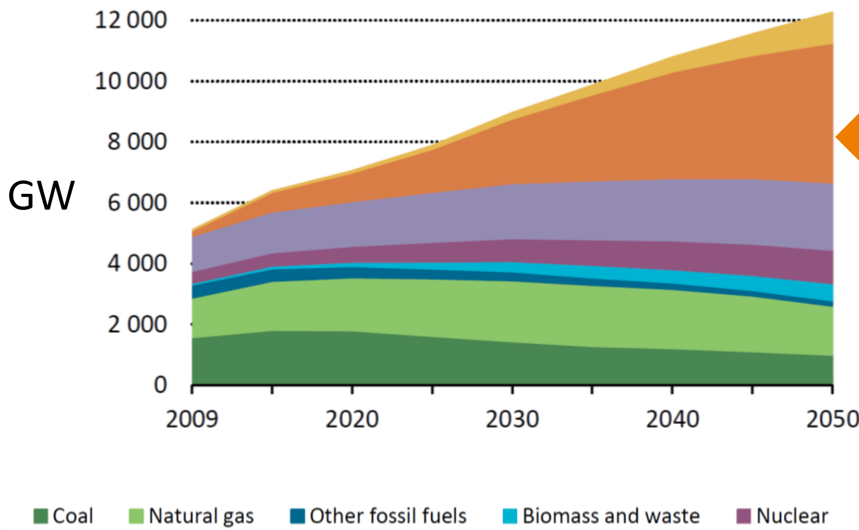
November 2014
ECN-L--14-083

POTENTIAL OF “POWER TO GAS” CONVERSION CHAIN INTEGRATION WITH BIOMETHANE PRODUCTION

M. Sarić, J.W. Dijkstra, S. Walspurger, W.G. Haije

ICCE2014
20- 22 October, 2014,
Quebec City

The future global electricity mix



Increasing share of variable renewables,
➔ Need for large electricity storage

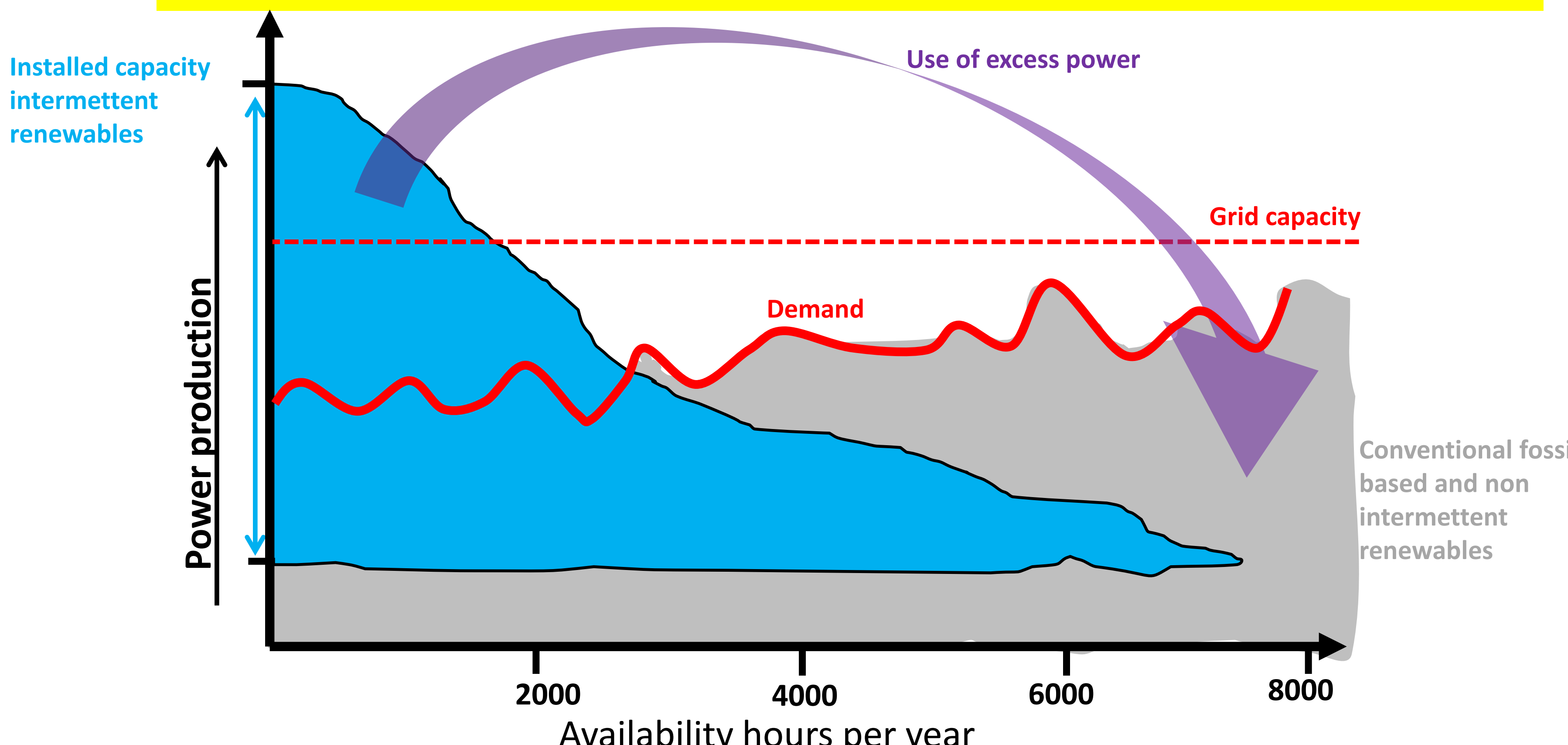
Source: IEA ETP, 2012

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

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

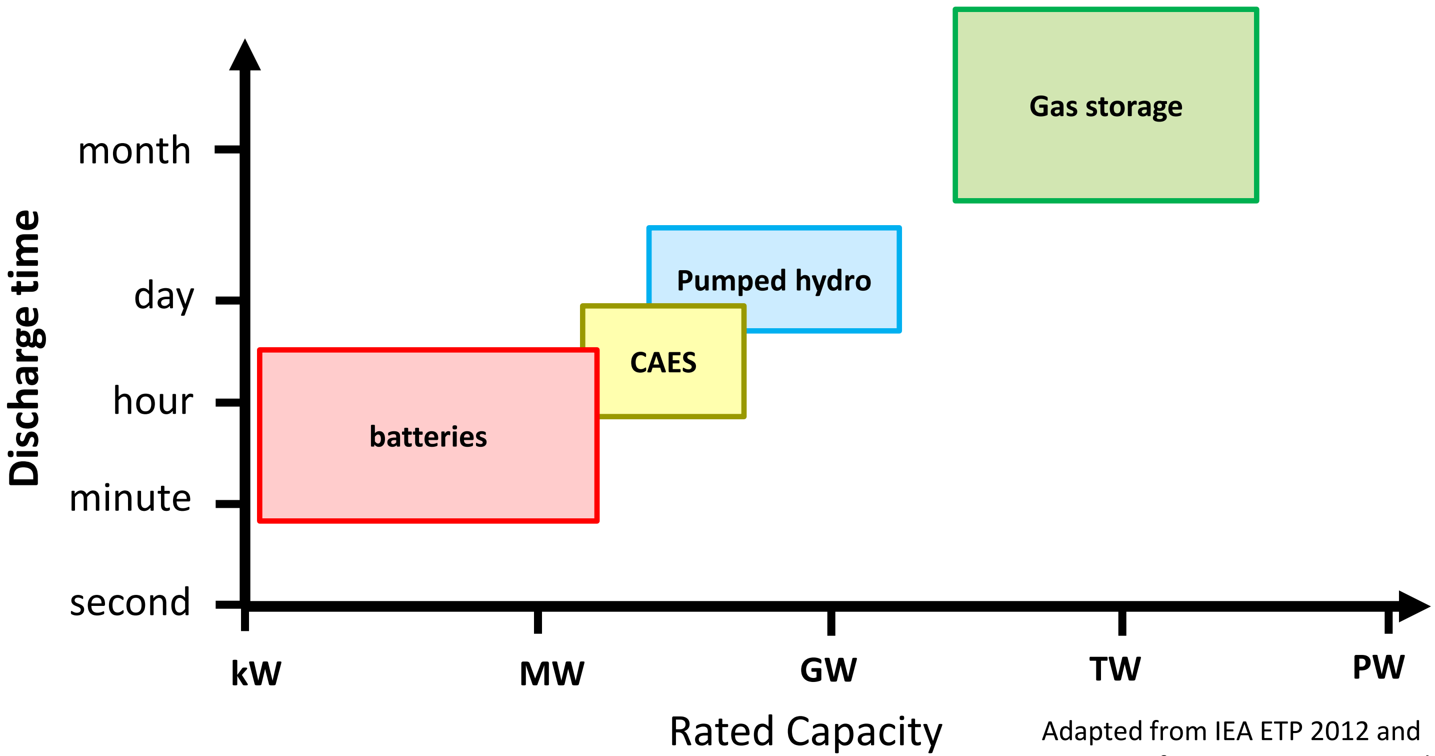
} Excess renewable electricity

Towards storing the excess power from renewables



Adapted from DVGW, Jurgen Lenz

Storage technologies



Adapted from IEA ETP 2012 and
Zentrum für Sonnenenergie und Waterstoff

Power to Gas routes

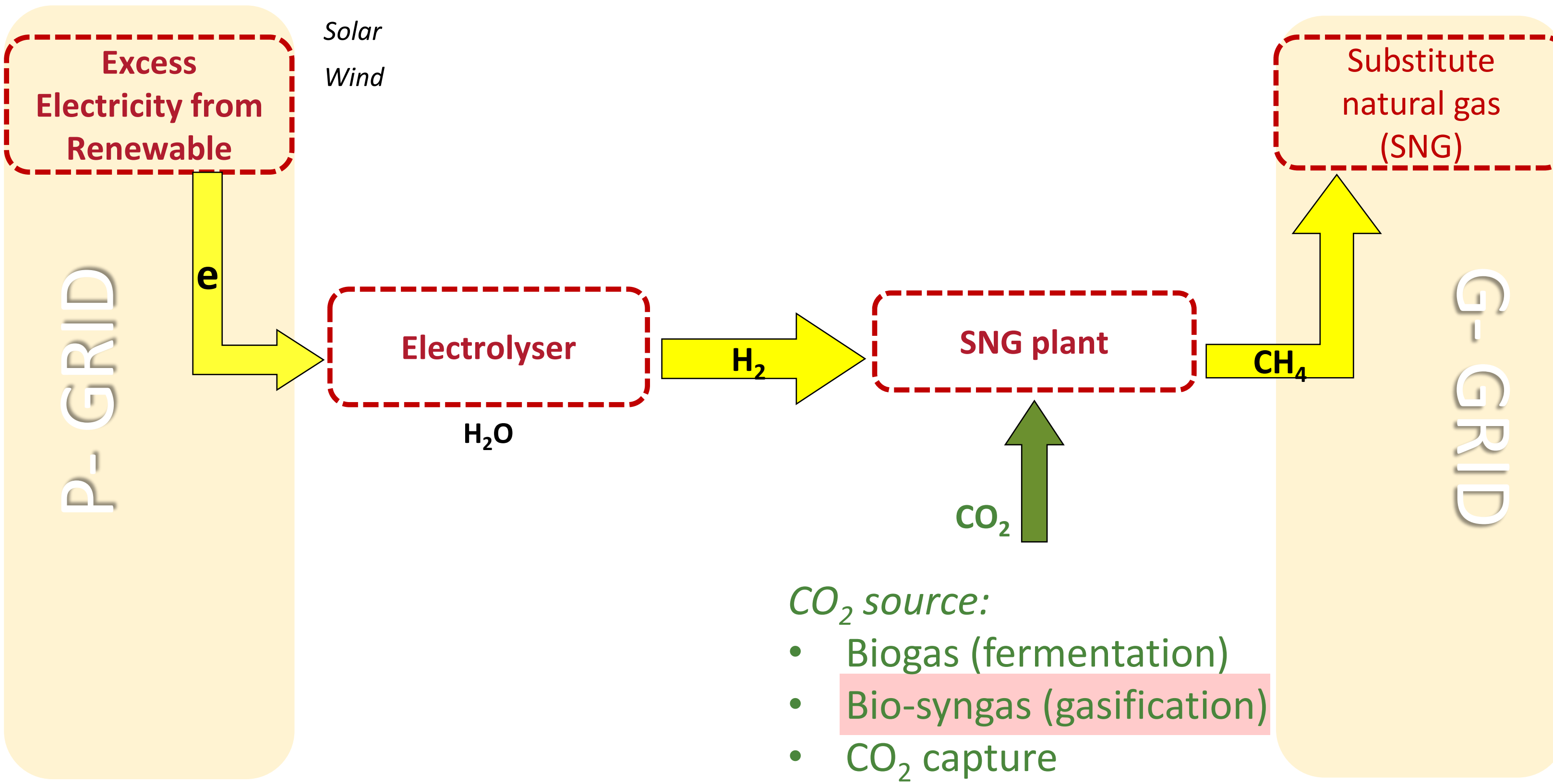
- Power to Hydrogen by electrolysis

Pros	Cons
Direct conversion (electrolysis)	Storage
No carbon	Distribution
Load Flexibilty	

- Power to Substitute Natural Gas by electrolysis + methanation

Pros	Cons
Existing infrastructure	Multistep process (efficiency)
CO_2 utilisation	
Energy density	

Power-to-(Green)-Gas



CO_2 source:

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

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

Objectives

Process

1. Configurations and conditions
2. Flexibility impact

Gas quality

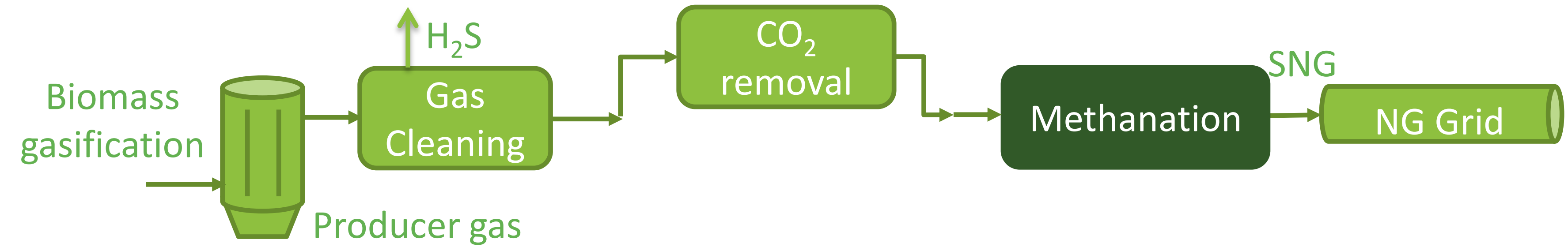
1. Thermodynamic assessment
2. Experimental
3. Novel process

Take home messages

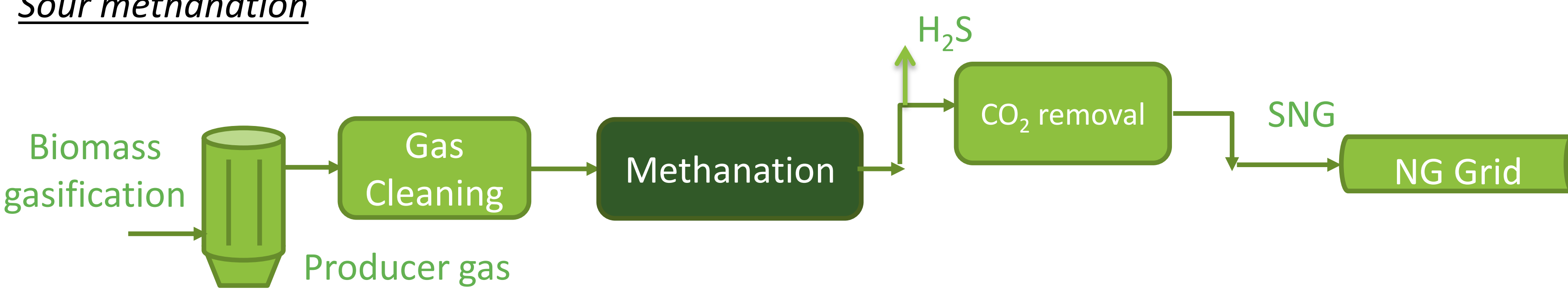
- Power-to-gas for producer gas upgrade can almost double SNG production
- Low impact on SNG quality, H_2 limit in the grid point of attention
- “Proof of principle” with novel sorption enhanced (SE)-methanation, close to 100% conversion

Systems modes evaluated: *E-demand*

<u>*Sweet methanation*</u>

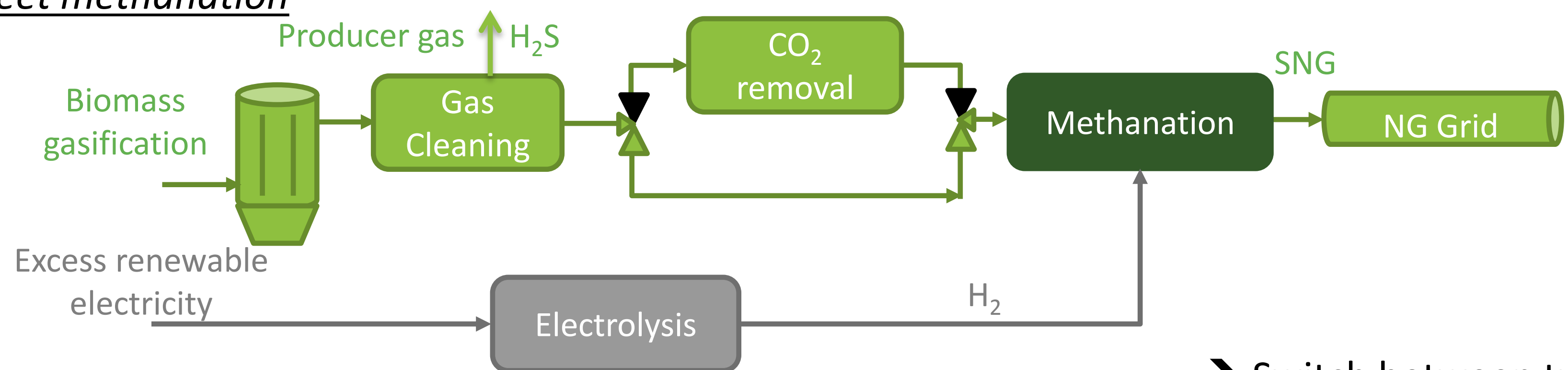


<u>*Sour methanation*</u>



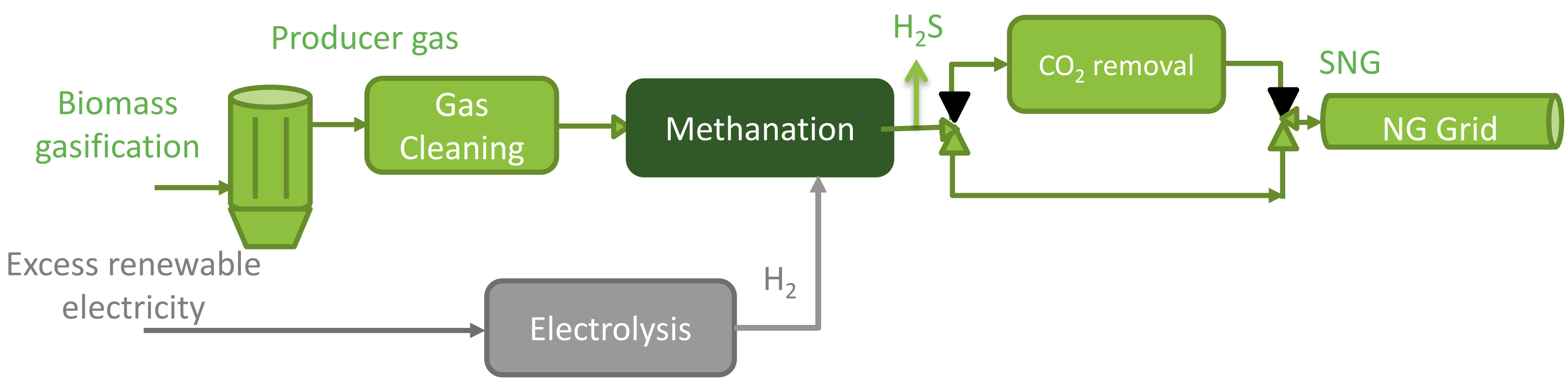
Systems modes evaluated: *E-excess*

Sweet methanation



➔ Switch between two modes

Sour methanation



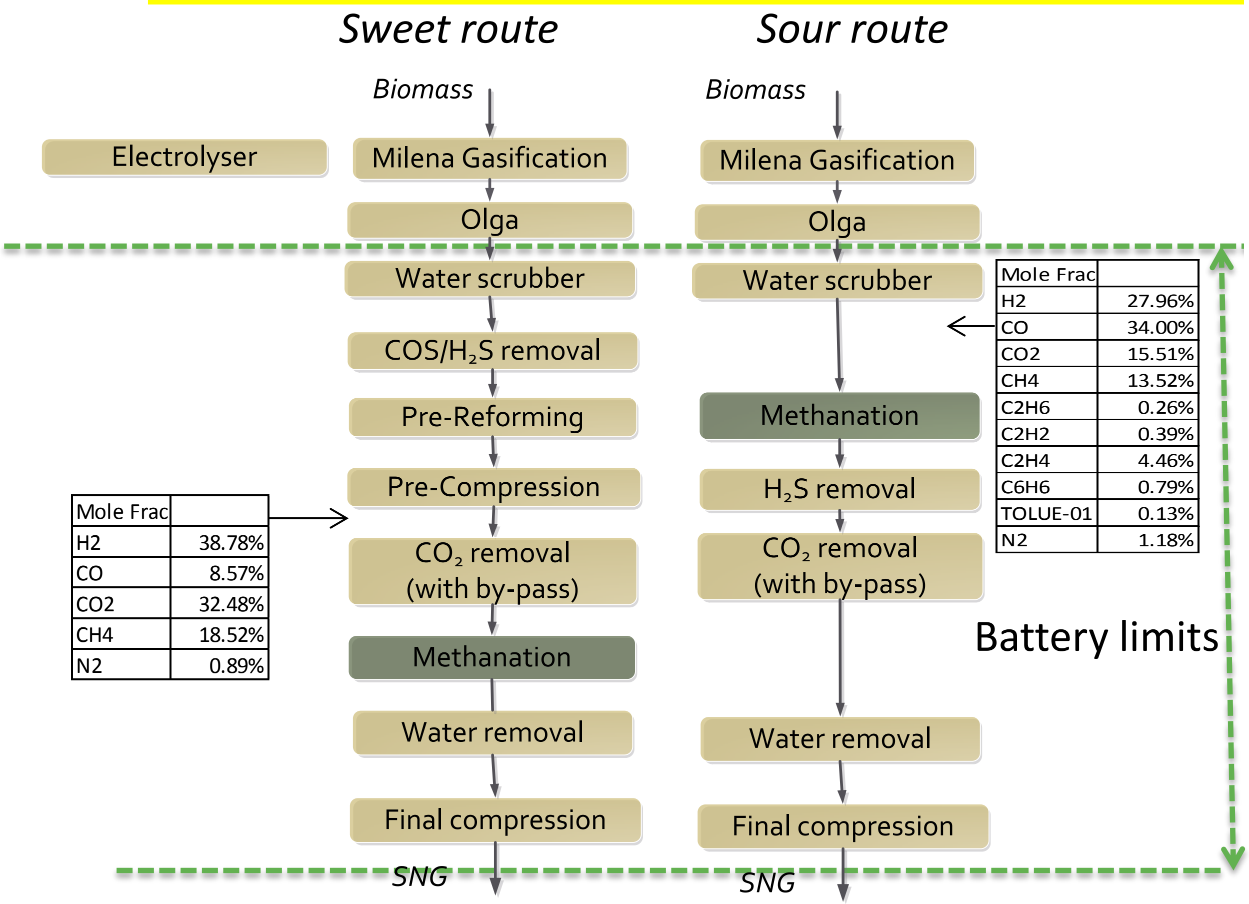
Sweet/Sour methanation differences

Sweet methanation	Sour methanation
(O)Stoichiometric ratio required	(+) Can operate under sub-stoichiometric conditions *
(-) Deep H_2S removal	(+) Less deep H_2S removal
(-) More process steps	(+) Less process steps (hydrogenates unsaturated hydrocarbons and reforms BTX)
(+) Commercially proven	(-) Limited commercial experience

*Lee, A. L. (1978) Evaluation of coal conversion catalysts.

ECN

System starting points



Mole Frac	
H2	38.78%
CO	8.57%
CO2	32.48%
CH4	18.52%
N2	0.89%

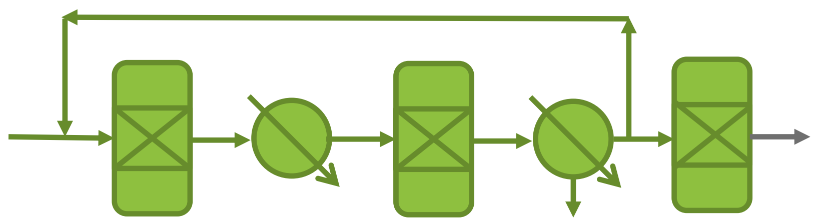
Mole Frac	
H2	27.96%
CO	34.00%
CO2	15.51%
CH4	13.52%
C2H6	0.26%
C2H2	0.39%
C2H4	4.46%
C6H6	0.79%
TOLUE-01	0.13%
N2	1.18%

800 kW MILENA pilot gasifier

Methanation section

Configuration:

multi-stage process with 3 intercooled fixed bed reactors



High temperature T_{max}=650°C, 3 stage, recycle after 2nd stage (LURGI HT)

Design variable:

Operating 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

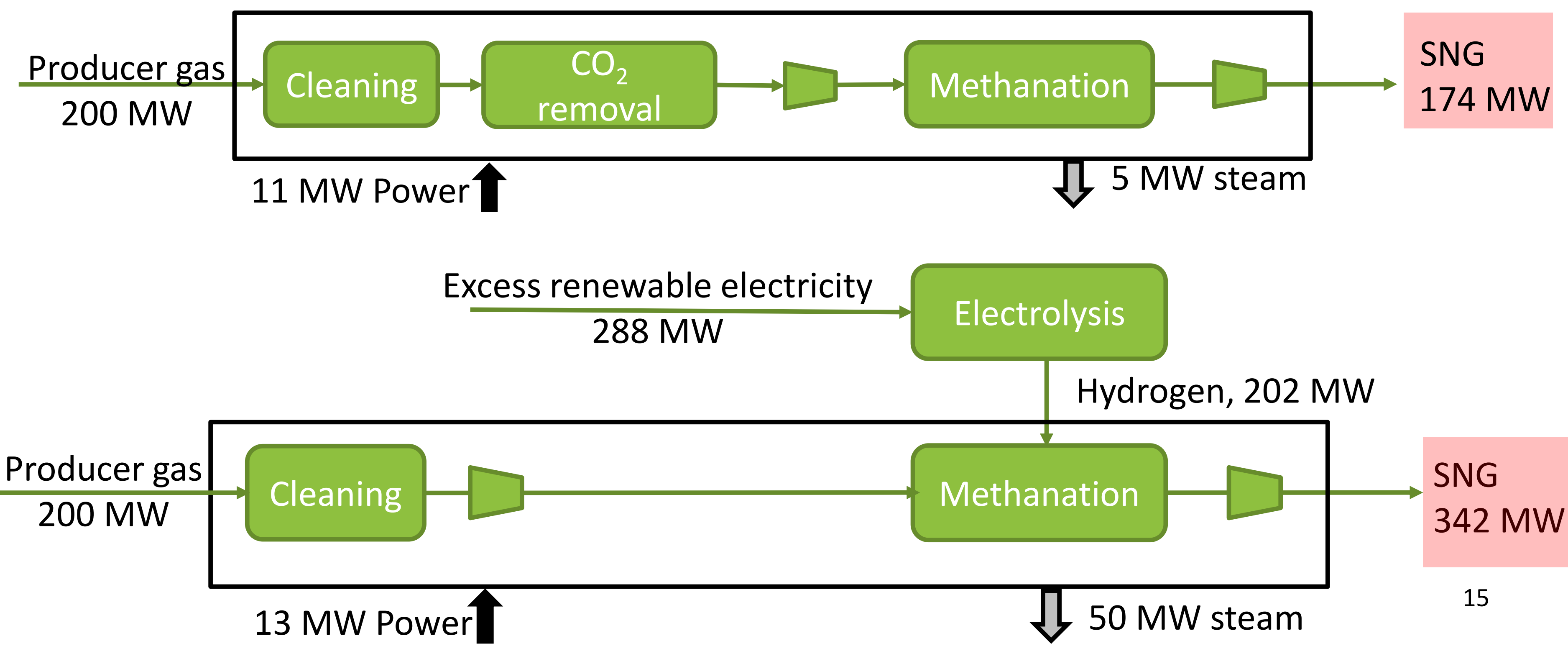
SNG molar H_2 Content

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

Energy balance

- Steam balance
- Total power use

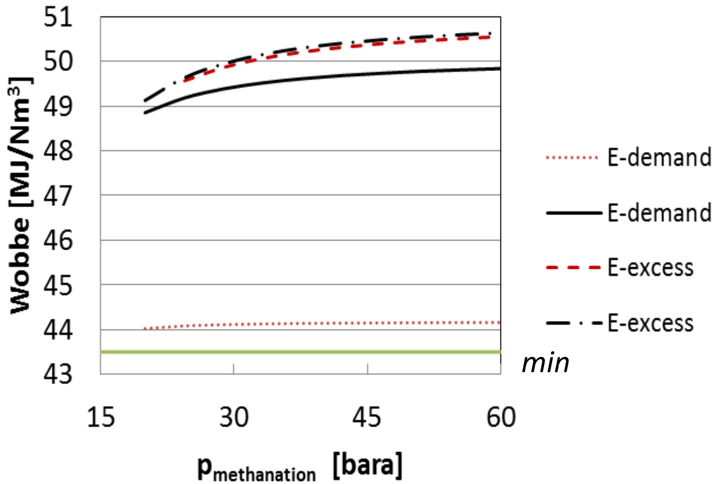
Comparison: *E-demand* vs. *E-excess (Sweet)*



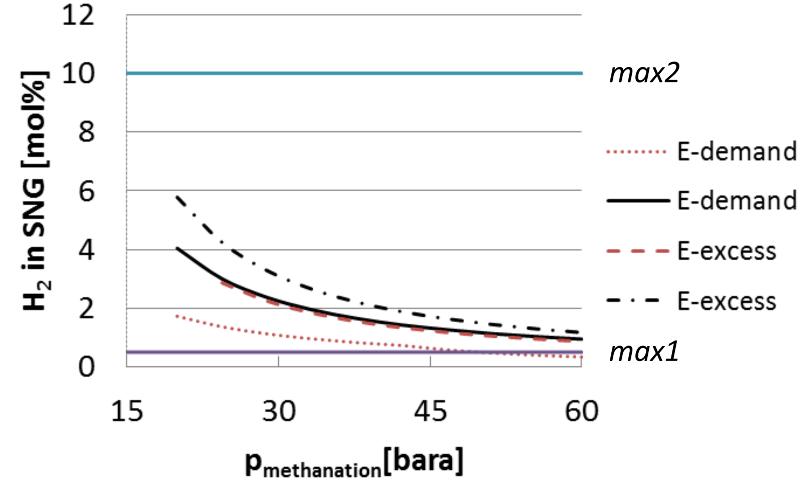
- ❑ Sour methanation comparable results

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

Wobbe always reached



Red – sour
Black –sweet

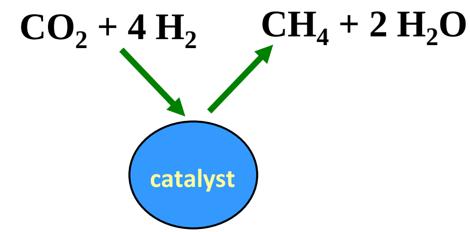


H_2 addition in *E-excess* has low impact on the gas quality

Sorption Enhanced (SE-)Methanation

CO_2 Methanation reaction

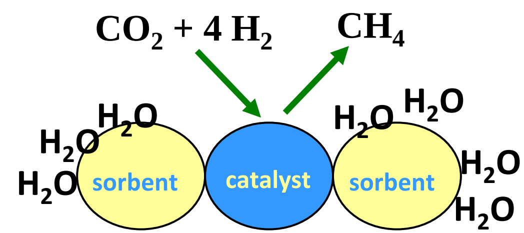
$CO_2 + 4\ H_2 \Leftrightarrow CH_4 + 2\ H_2O$



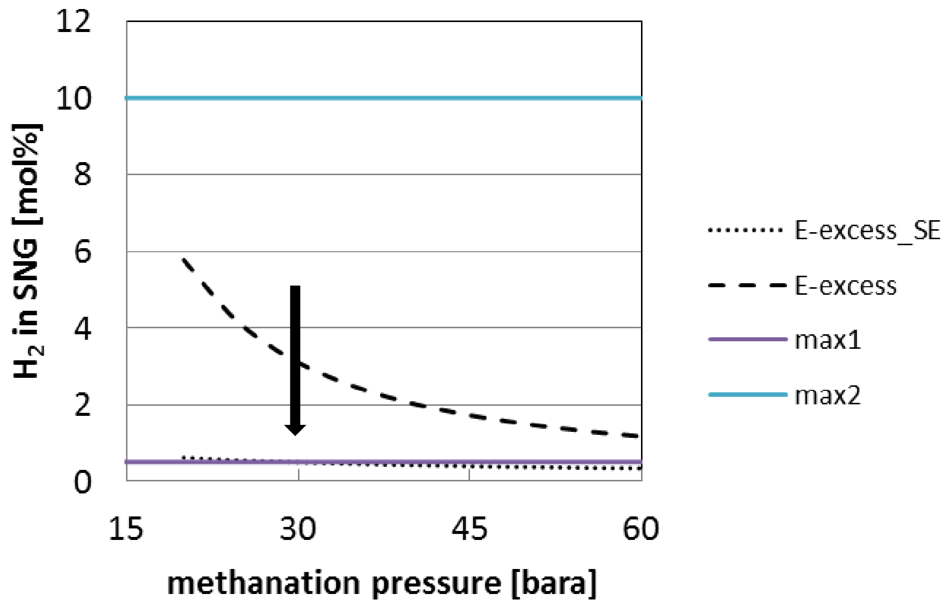
CO_2 Methanation reaction + Water removal

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

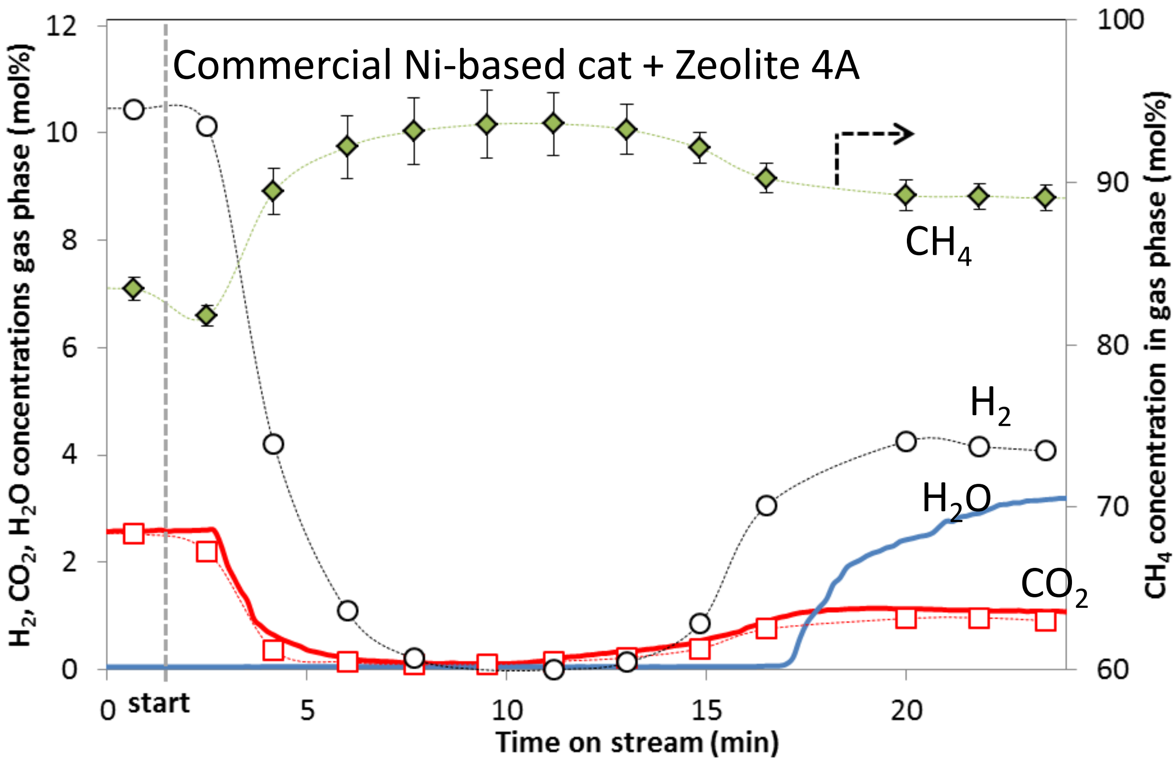
Conclusions & Outlook
System studies

- Power-to-gas is a flexible solution that can double the SNG production
- *Sweet* and *Sour* methanation similar performance. *Sour* more interesting due to anticipated less process steps.
- 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 CO_2 sources (captured CO_2, biodigester gas, other industrial processes)

Experimental results SE-methanation

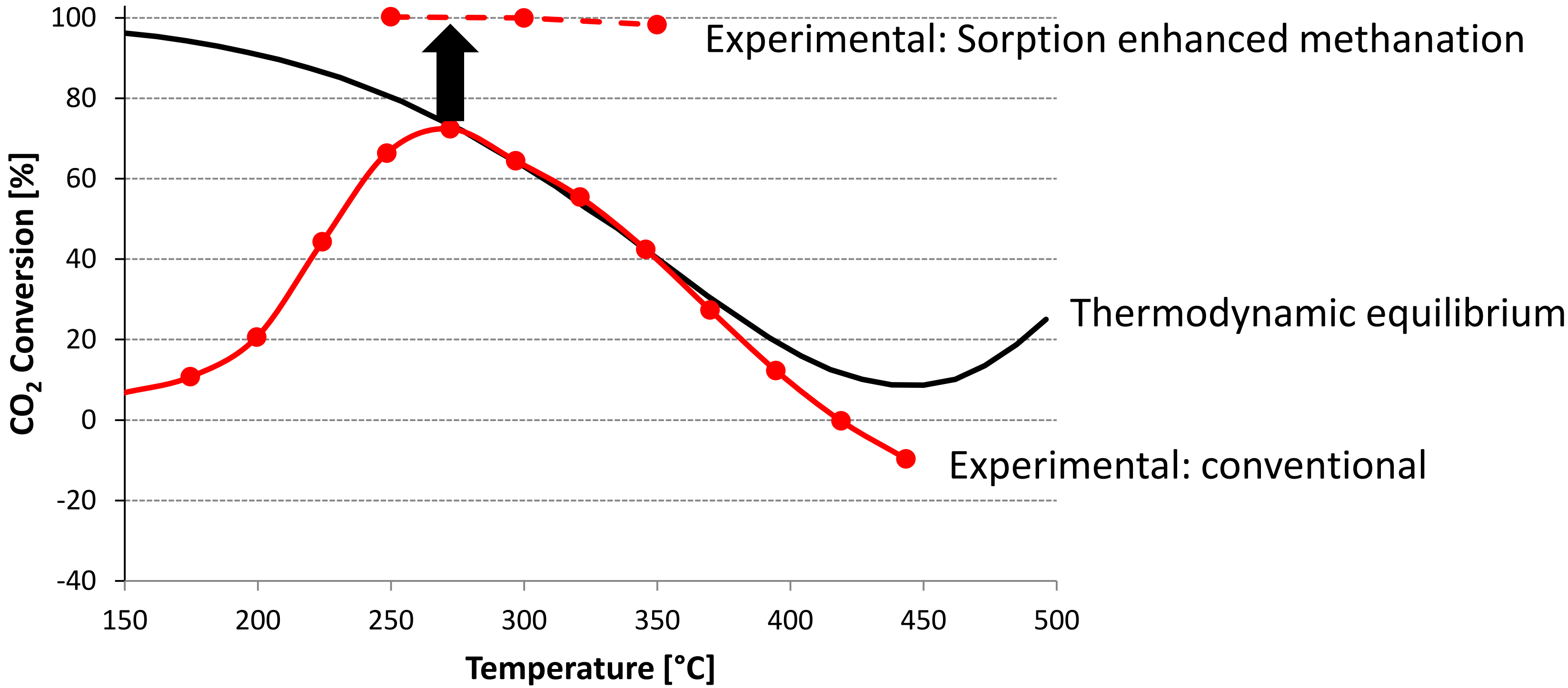


Inlet composition:
2.5% CO_2, 9.9% H_2, 81.6%CH_4, and 6%N_2
P = 1 atm, total flow = 150 ml/min,
T=250°C, 3.6 g (Zeolite 4A:cat=5:1)
Regeneration: N_2 and H_2

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

*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

ECN

- 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
- "Proof of principle" with novel sorption enhanced (SE)-methanation, close to 100% conversion
- Power to gas can be used for other CO_2 sources (captured CO_2, biodigester gas, other industrial processes)

EDGAR Synthetic methane project

SOE, Solid Oxide Electrolyzer (TUD)

- Characterization, modeling and development

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

Acknowledgements

The research program EDGaR acknowledges the contribution of the funding agencies: The Northern Netherlands Provinces (SNN). This project is co-financed by the European Union, European Fund for Regional Development and the Ministry of Economic Affairs, Agriculture and Innovation. Also the Province of Groningen is co-financing the project.

EDGaR Synthetic Methane project partners

ECN

Westerduinweg 3
1755 LE Petten
The Netherlands
T +31 88 515 49 49
F +31 88 515 44 80

P.O. Box 1
1755 ZG Petten
The Netherlands
info@ecn.nl
www.ecn.nl

Publications: www.ecn.nl/publications
Fuel composition database: www.phyllis.nl
Tar dew point calculator: www.thersites.nl
IEA bioenergy/gasification: www.ieatask33.org
Milena indirect gasifier: www.milenatechnology.com
OLGA: www.olgatechnology.com / www.renewableenergy.nl
SNG: www.bioSNG.com /www.bioCNG.com

ECN

Westerduinweg 3
1755 LE Petten
The Netherlands

P.O. Box 1
1755 LG Petten
The Netherlands

T +31 88 515 4949
F +31 88 515 8338
info@ ecn.nl
www.ecn.nl