# Advanced Green Gas Technology (AGATE), phase 1

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# Advanced Green Gas Technology (AGATE), phase 1

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EDGaR Energy Delta Gas Research

university of groningen

# AGATE1 partners, contacts & subjects

| | | |
|---|---|---|
| • ECN | Luc Rabou | Dry biomass gasification => methane |
| • RUG ST/OC | Erik Heeres | Wet biomass gasification => methane |
| • RUG CIO | Sanne Palstra | $^{14}C$ analysis for “green” gas |

Project finished December 2013

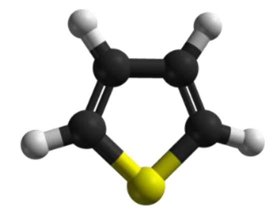
ECN and RUG ST/OC research continues in AGATE2

# ECN R&D in AGATE1

- Construction of pressurised test rig for conversion of organic sulfur
- Reforming of aromatic hydrocarbons (*HDS = HydroDeSulfurization*)
- Gas cleaning tests

WHY?

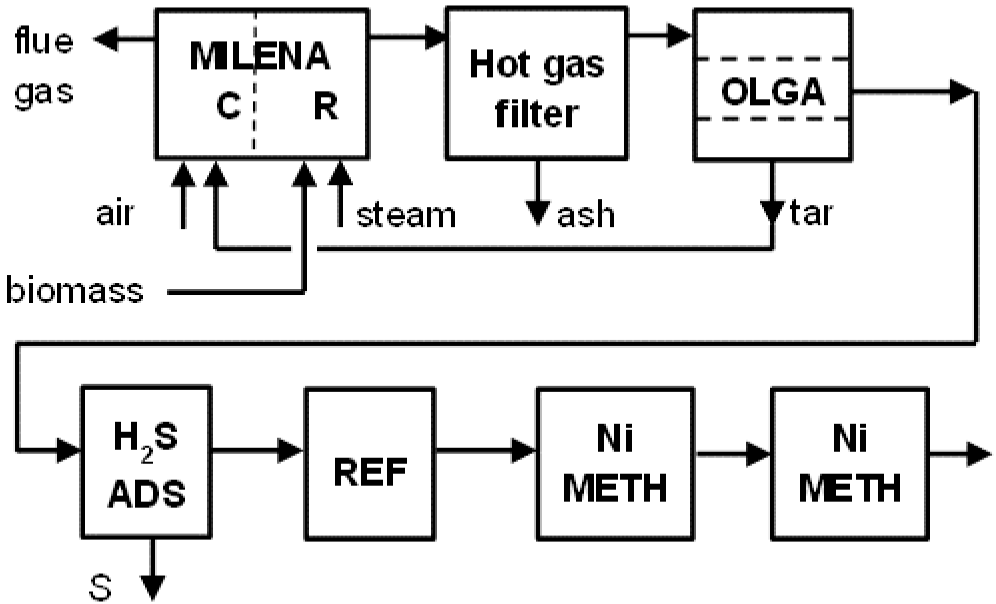
**Groen Gas 2.0**
**Milena-Olga-SNG**



- Org-S (mainly $C_4H_4S$) poisons methanation catalyst

  HDS slow at 1 bar; methanation requires high pressure
- Aromatic hydrocarbons => coke deposit, catalyst deactivation
- Assess performance

# State of ECN R&D in 2010




| | |
|---|---|
| Gasifier | (MILENA) |
| Dust removal | (filter) |
| Tar removal | (OLGA) |
| $H_2S$ removal | (SACHA) |
| $C_xH_y$ reformer | (SNG) |
| Methanation | (SNG) |

*At atmospheric pressure*

# ECN test rig in 2010

MILENA

OLGA

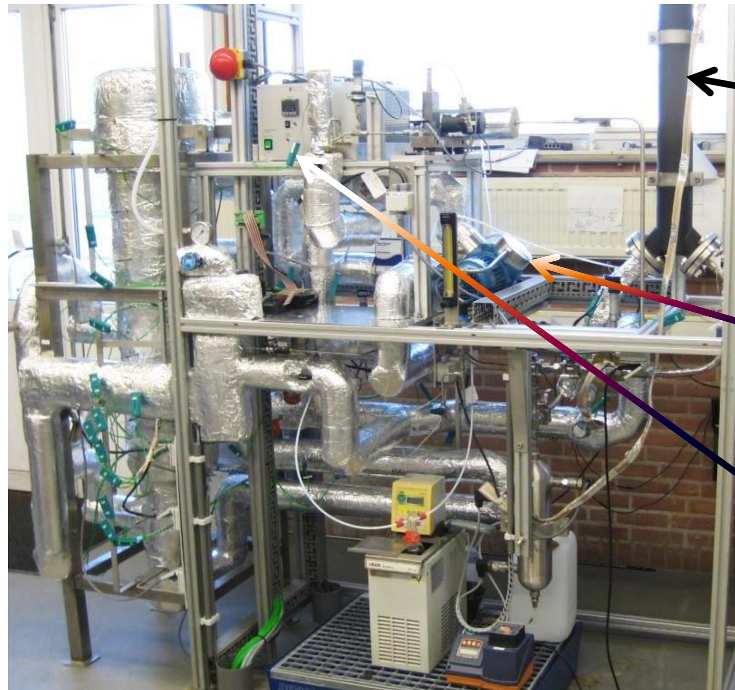
SACHA

SNG

# ECN pressurised HDS test rig

Gas sampling lines

HDS side view



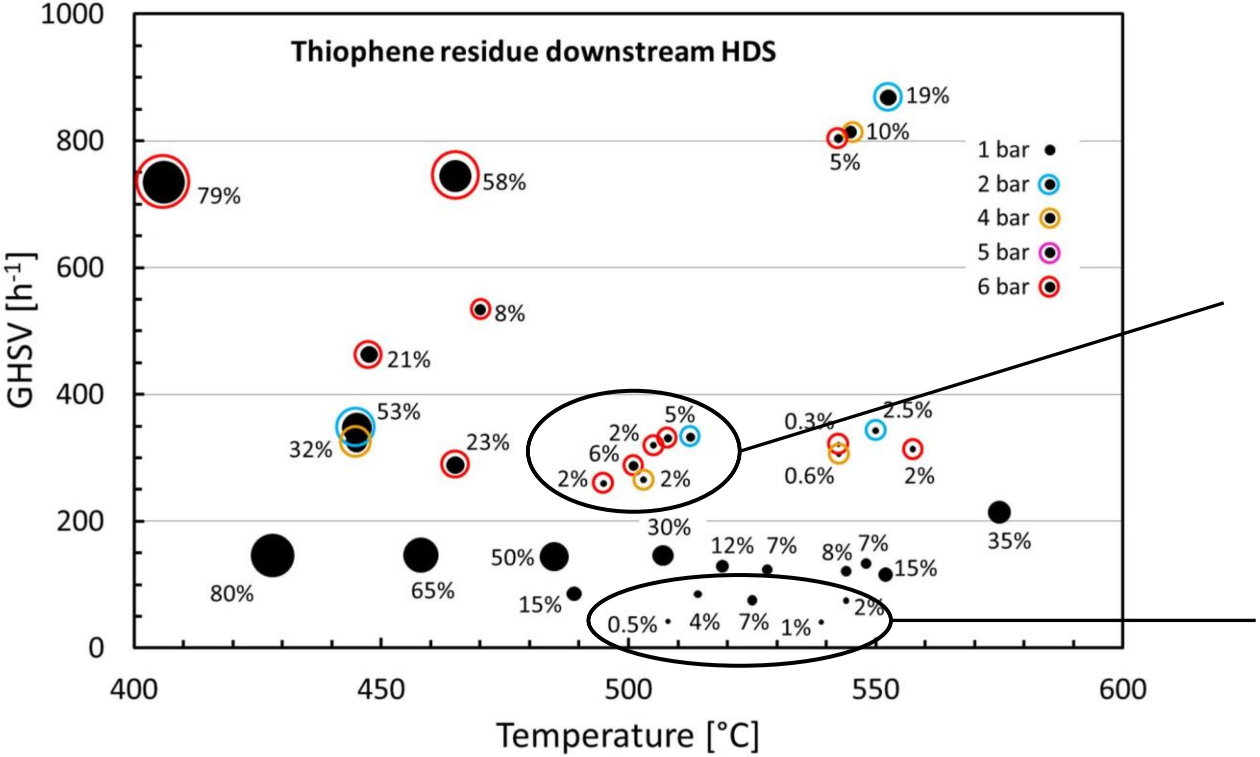
Heat exchanger for cooling/drying of gas from OLGA

Compressor

Steam generator

HDS rig front view

# HDS results: thiophene conversion




Lower temperature & higher gas velocity allowed for >95% conversion at 6 bar

High temperature & low gas velocity required for >95% conversion at 1 bar

# Benzene reforming

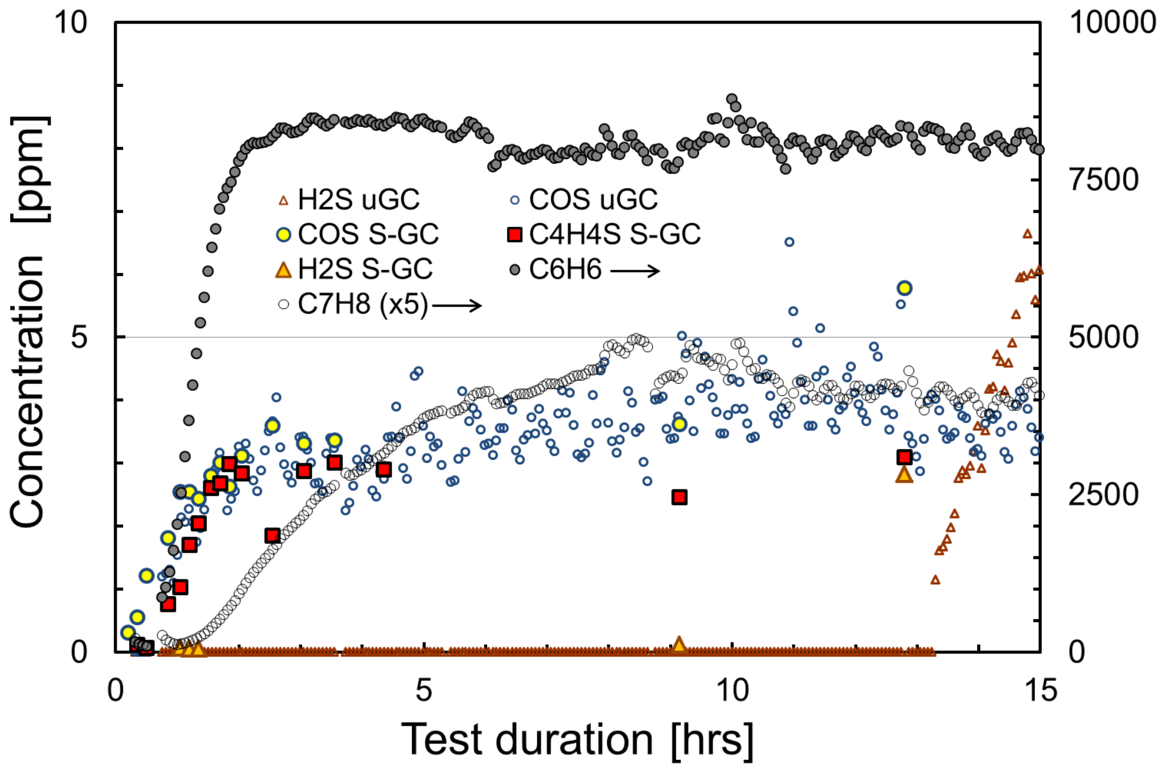

Microflow reactors with different catalysts:

amount of carbon deposit varies significantly

⇒ Catalyst selected for optimization of conditions

is continued in AGATE phase 2

# Thiophene adsorption by active carbon




Impregnated active carbon

Order of break-through:

- COS
- Benzene, thiophene
- Toluene
- $H_2S$

# Conclusions of ECN research

Conversion of thiophene improves with pressure

HDS reactor size comparable to size of methanation reactors

Benzene reforming requires further research (in AGATE phase 2)

Thiophene adsorption possible, but has to compete with BTX

BTX + thiophene removal still an option (studied in SNG Impact)

# RUG ST/OC R&D in AGATE1

- Supercritical gasification in water (SCWG) batch experiments
- Construction test rig for continuous SCWG experiments
- SCWG continuous experiments

WHY and HOW?

- High conversion of wet biomass to $CH_4$
- Comparison of heterogeneous catalysts and catalyst nanoparticles
- From simple organic compound to more complex mixture

# Batch SCWG: reactor

Tests at ~250 bar and 400°C

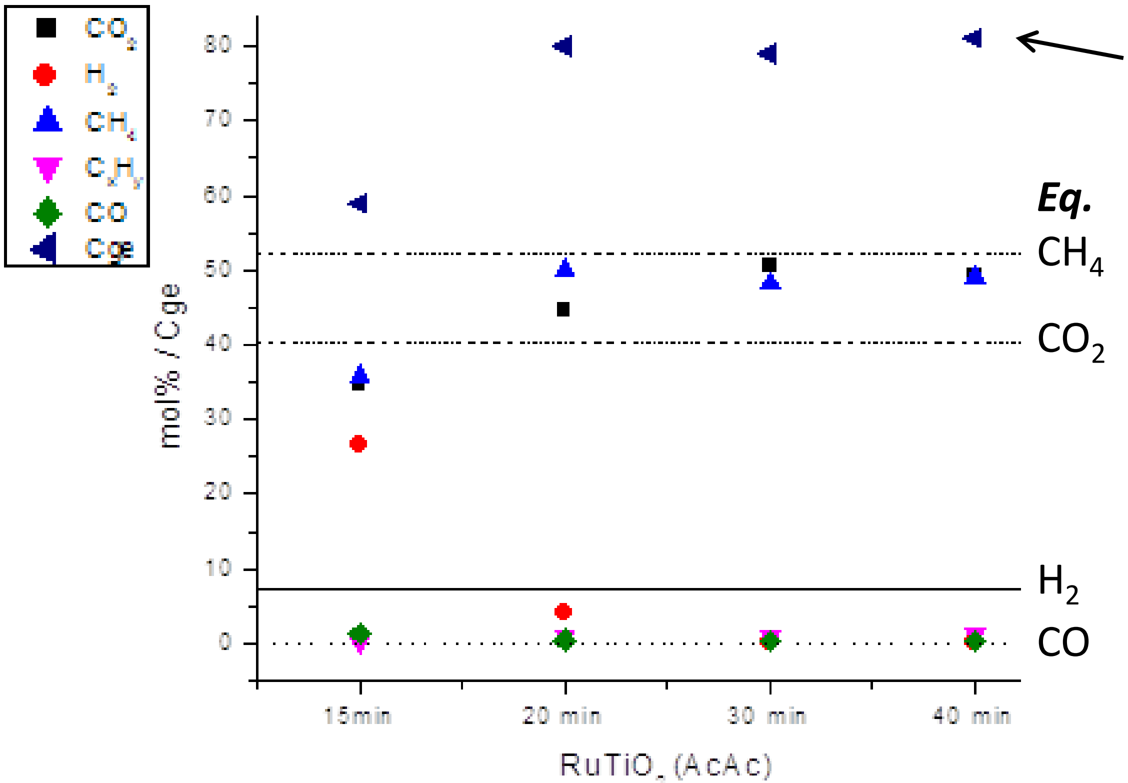
Volume 14 ml

Glycerol in water

Several Ru and Ni catalysts

- commercial or home made
- powder or nanoparticles

# Batch SCWG: residence time

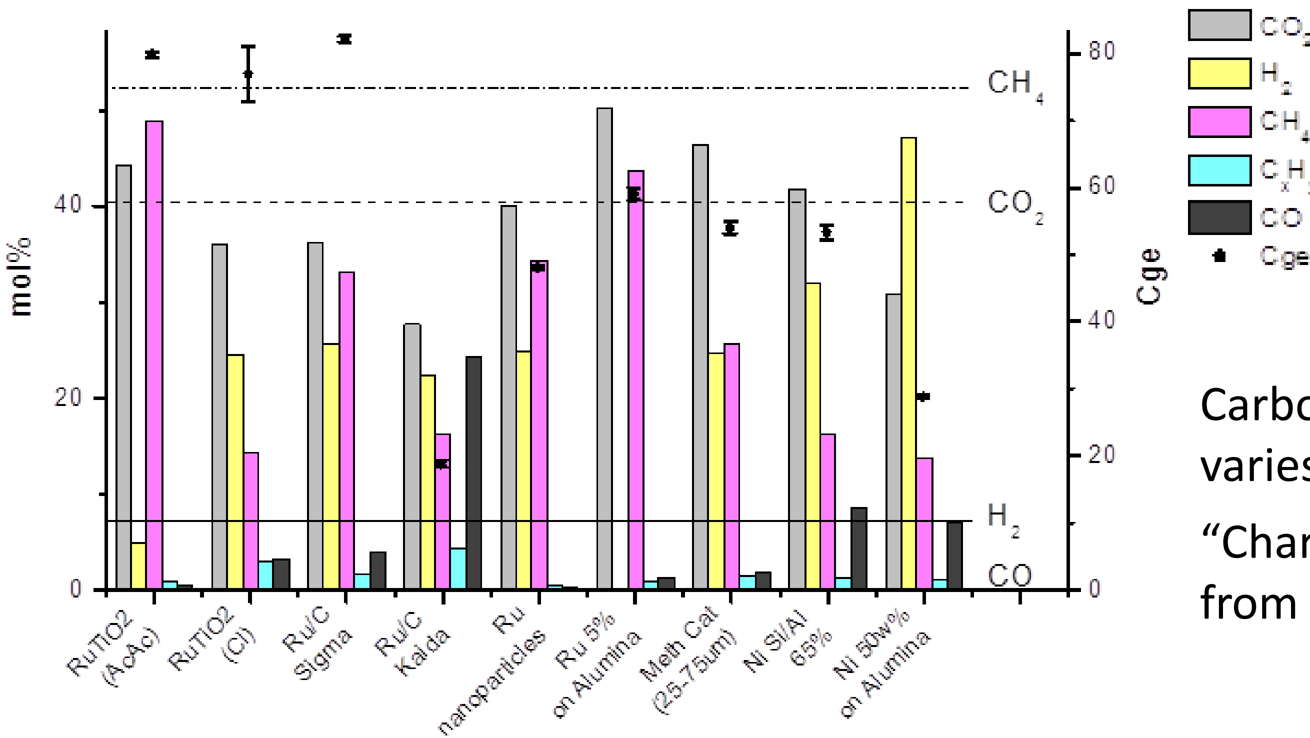



$$Cge = \frac{\text{carbon in gas}}{\text{carbon in feed}}$$

Gas composition close to equilibrium in 20 to 30 minutes

Maximum carbon to gas conversion in 20 minutes

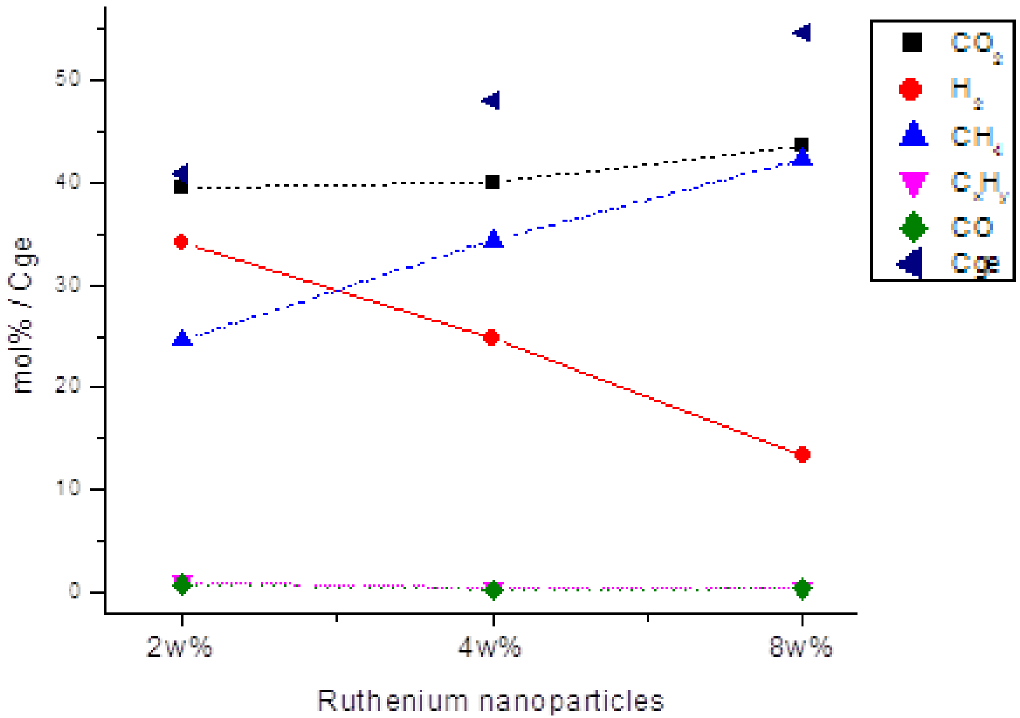
# Batch SCWG: gas composition & conversion




Carbon to gas efficiency varies from 19% to 82%

"Char formation" varies from 5% to 33%

# Batch SCWG nanoparticles




Limited conversion

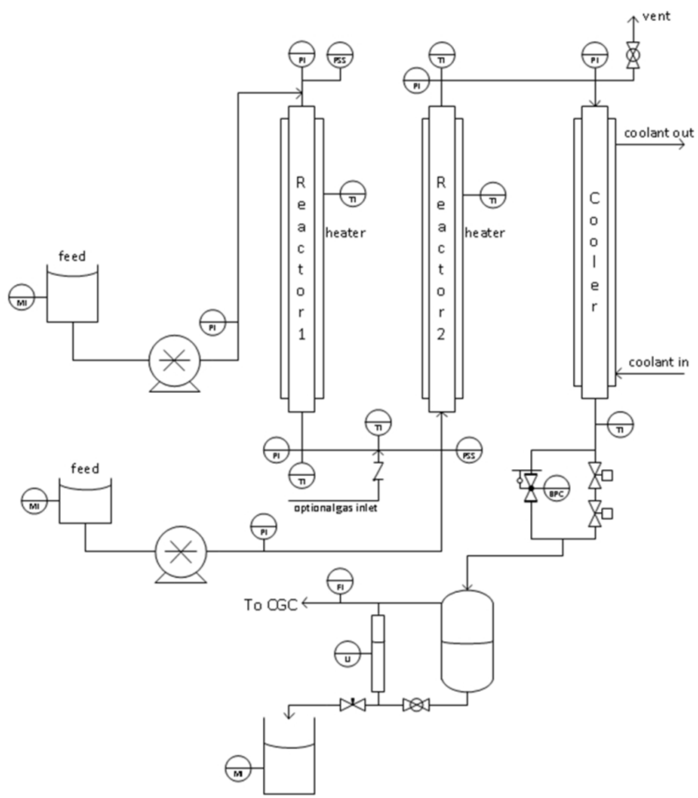
Gas composition does not reach equilibrium

Little improvement with residence time

Sintering and/or deposition of catalyst must be prevented

(research continues in AGATE2)

# Continuous SCWG: reactor



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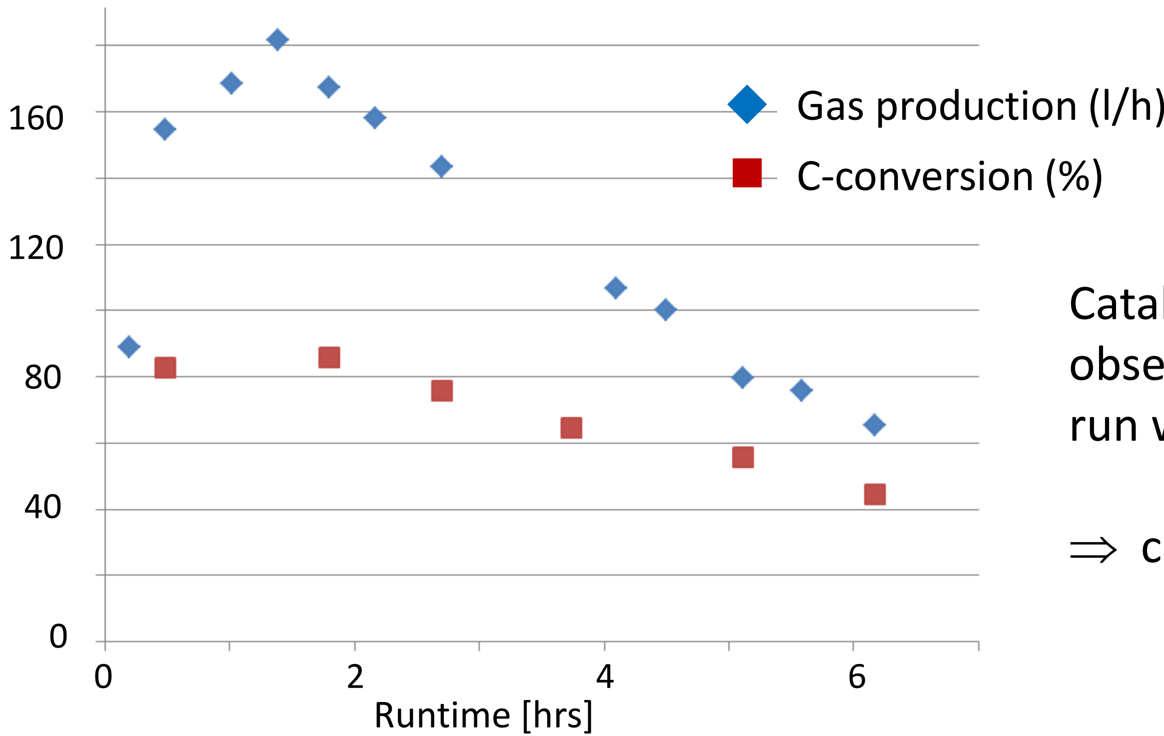
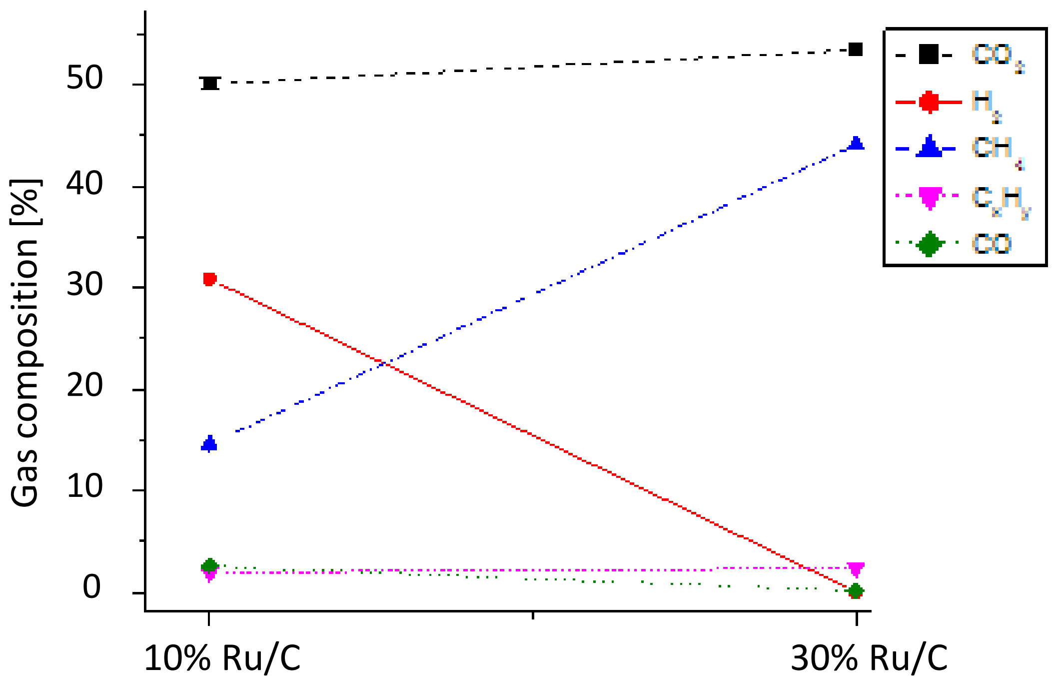
# Continuous SCWG: 0.5% Ru/C




Catalytic activity observed in next test run without catalyst

$\Rightarrow$ catalyst deposit on reactor wall

# Batch SCWG pyrolysis oil




Carbon to gas conversion lower than for glycerol (10% instead of 80%)

Higher temperature may increase conversion but will reduce $CH_4$ content

# Conclusions of RUG-ST/OC research

80% conversion of glycerol to gas

Gas composition close to equilibrium,

i.e. nearly pure $CH_4/CO_2$ at 400°C 250 bar

$Ru/TiO_2$ best performing catalyst

Stability of (nanoparticle) catalysts needs improvement

Conversion of pyrolysis oil more difficult

# RUG CIO R&D in AGATE1

- Develop $^{14}C$ analysis method for natural gas, biogas and SNG

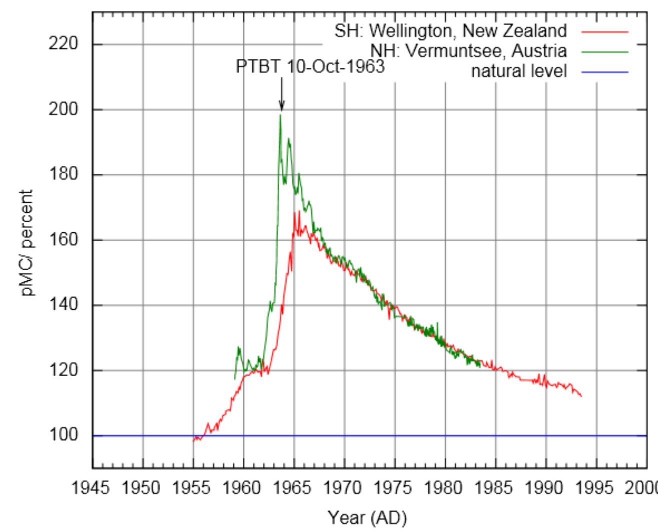
WHY and HOW?

- Allow check of origin (i.e. fossil and/or biomass signature)
- Is already used for waste combustion, based on $CO_2$ capture

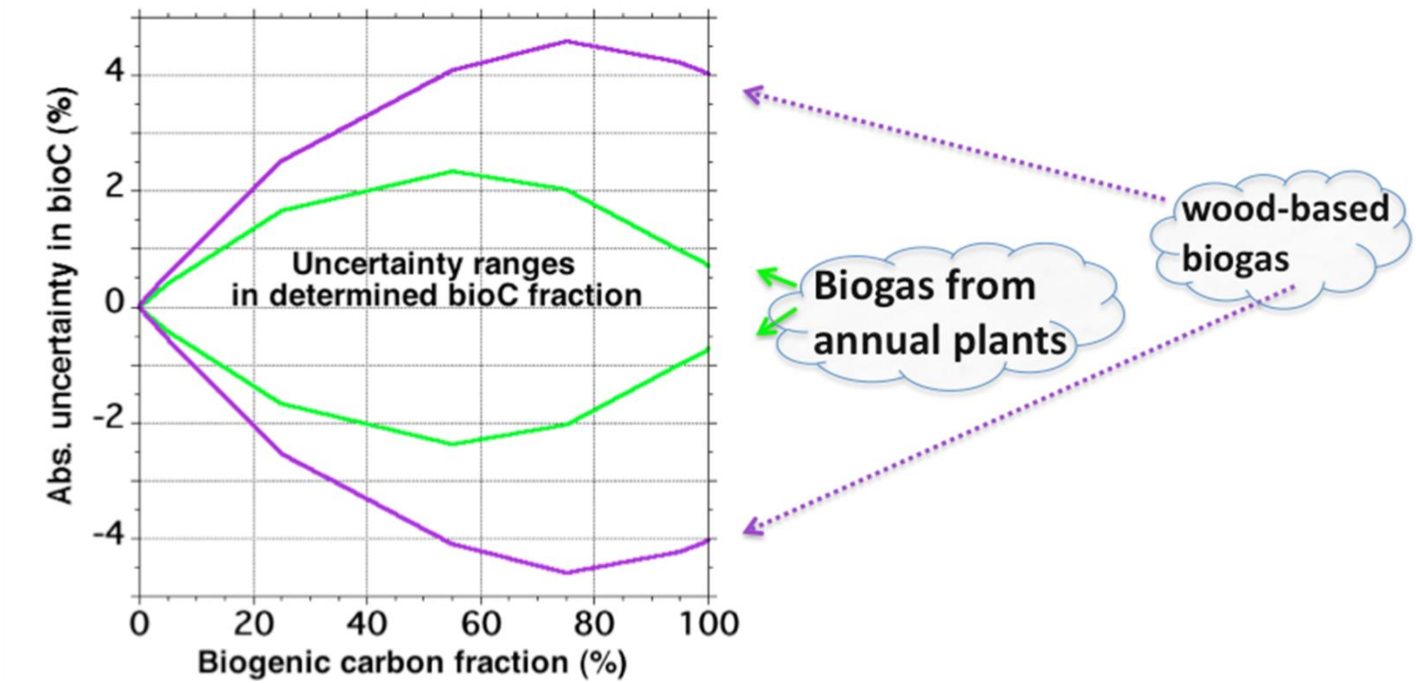
  => combustion of natural gas/biogas/SNG, followed by "standard" analysis

# Obstacles in $^{14}C$ analysis

- $^{14}C$ content in biomass varies with year of growth
    - Background from nuclear reactions by cosmic rays
    - Peak levels from above-ground nuclear tests
- $^{14}C/^{12}C$ disproportionation => compare $^{13}C/^{12}C$
- $CH_4$ and $CO_2$ in biogas or SNG may have different signatures => separate before combustion
- ECN test rig gases also contain CO, $C_2H_4$ etc.



# Uncertainty in $^{14}C$ analysis



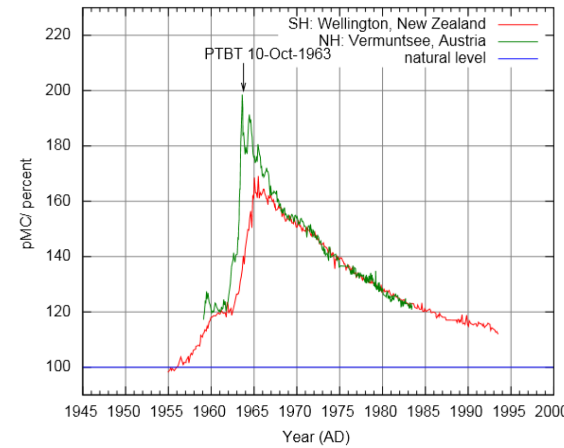
# Results (1)

- Quantitative separation, combustion and recovery of $C_2H_4$ and CO difficult
- Equipment built for separation and combustion of $CH_4$ (and $C_2H_6$) from $CH_4/C_2H_6/CO_2$ mixtures
- 3 natural gas and 8 biogas samples analysed

  => good agreement between $^{14}C$ signals from $CO_2$ and $CH_4/C_2H_6$ part:

  0-1 pMC *(% modern carbon*) for natural gas, i.e. no $^{14}C$

  102-105 pMC for biogas, 104 and 116 pMC for two landfill gas samples

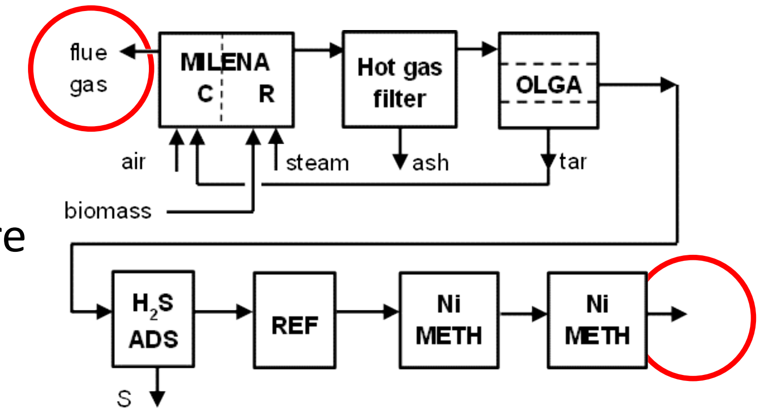


# Results (2)

- Flue gas & raw SNG from ECN test rig
- $^{14}C$ results identical when wood is gasified
- $^{14}C$ results different for wood/lignite mixture

  => SNG more biomass signature,

  flue gas more fossil signature



# Conclusions of RUG-CIO research

$^{14}C$ signature depends on biomass age (also true for waste combustion)

$^{14}C$ signature for biogas from annual crops accurate within a few percent

$^{14}C$ signature for landfill gas requires age correction

$^{14}C$ signature for SNG does reflect fuel signature in case of biomass, but not if a mixture of fossil fuel and biomass is used

A standard $^{14}C$ method for biogas and SNG requires further R&D

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