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Wir schaffen Wissen – heute für morgen

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Hydrothermal Gasification of Microalgae for Biomethane Production (SunCHem Process)

Outline

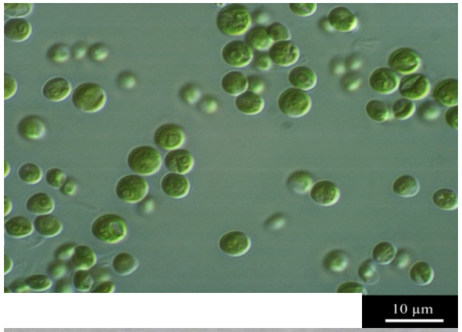
- Why microalgae as a bio-energy source? Why biomethane?
- Hydrothermal Gasification Process (SunCHem Process)
- Ru/C catalysts for CSCWG of isopropanol as organic model compound
- Conclusion and perspectives

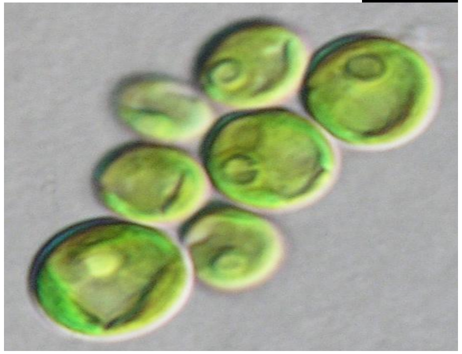
Why microalgae as a bio-energy source?

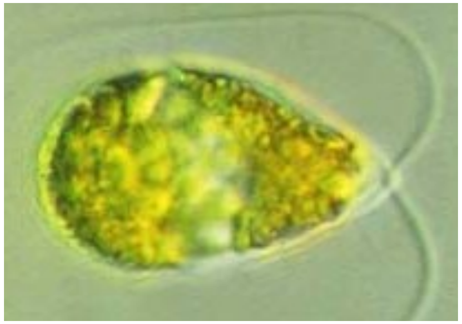
No competition with food crops (3th generation biofuels)

High photosynthetic efficiency and biomass production rates

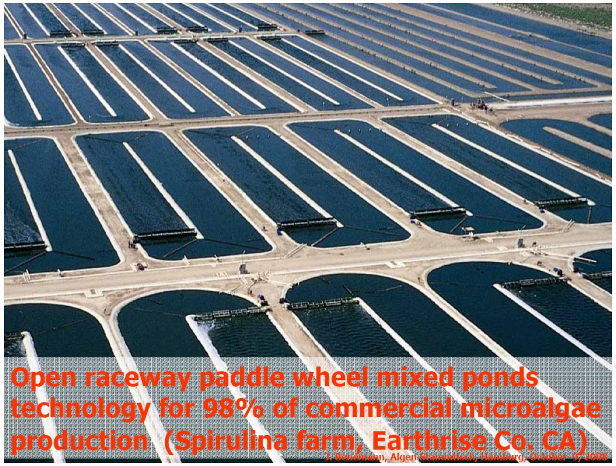
- Forest **8-12 t/ha/yr**
- Algae (open pond) similar to tropical agriculture **30 t/ha/yr**
- Algae (photobioreactor) > **150 t/ha/yr**







Algae supplier: SAG



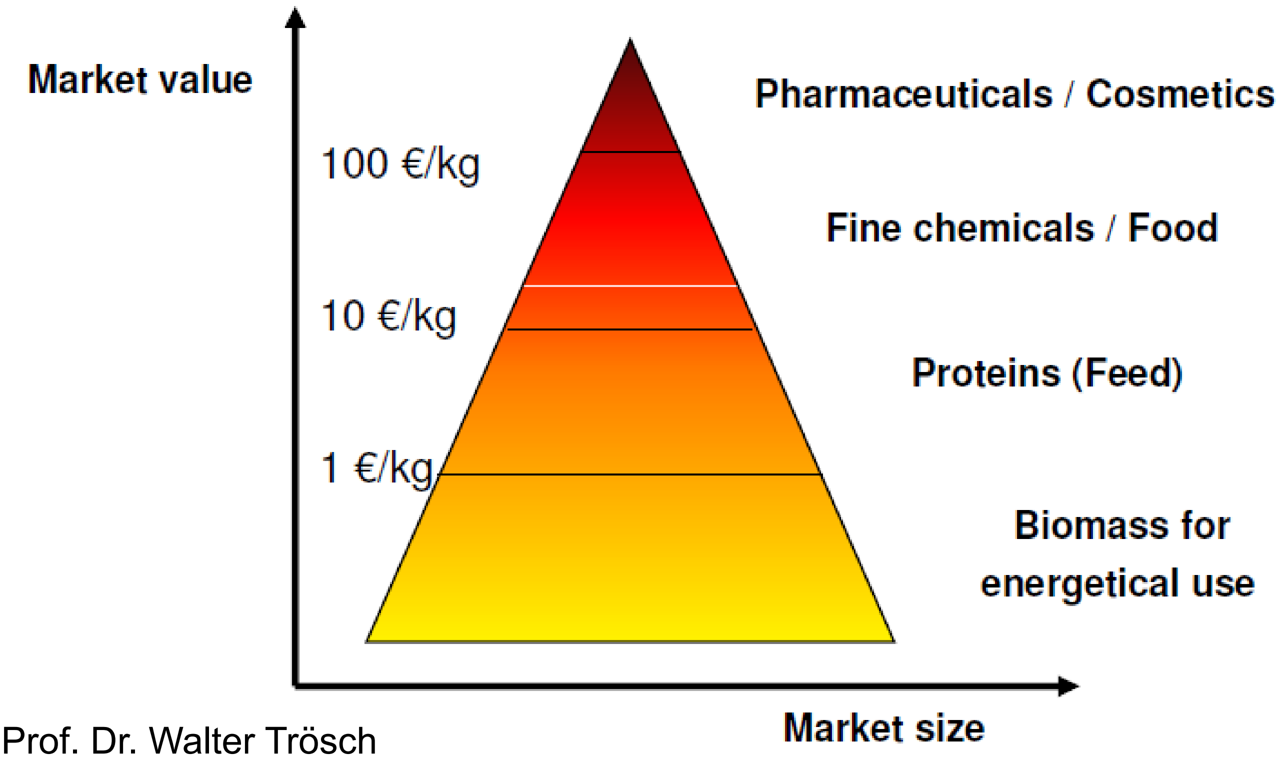
Open raceway paddle wheel mixed ponds technology for 98% of commercial microalgae production (Spirulina farm, Earthrise Co. CA)

Subitec, Eutingen-Weitingen

Why microalgae as a bio-energy source?

Poly generation pathways with production of **high cost chemicals**

- Lipids (PUFAs)
- Proteins
- Pigments (Carotenoids)



Why biomethane?

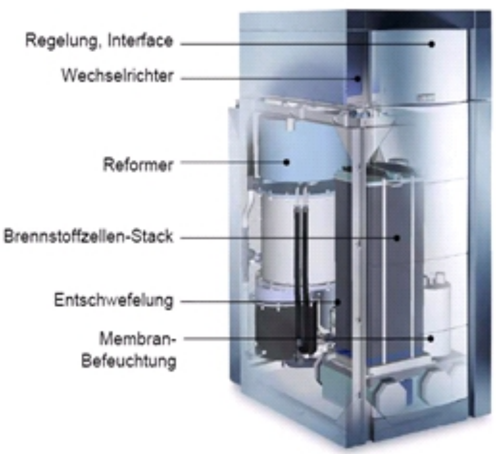
High diversity of use:

For Mobility, Household (SOFC), Plant (CHP)

plugpower

Vaillant

HEXIS



1-4.6 kW_{el}
1.5-7 kW_{th}

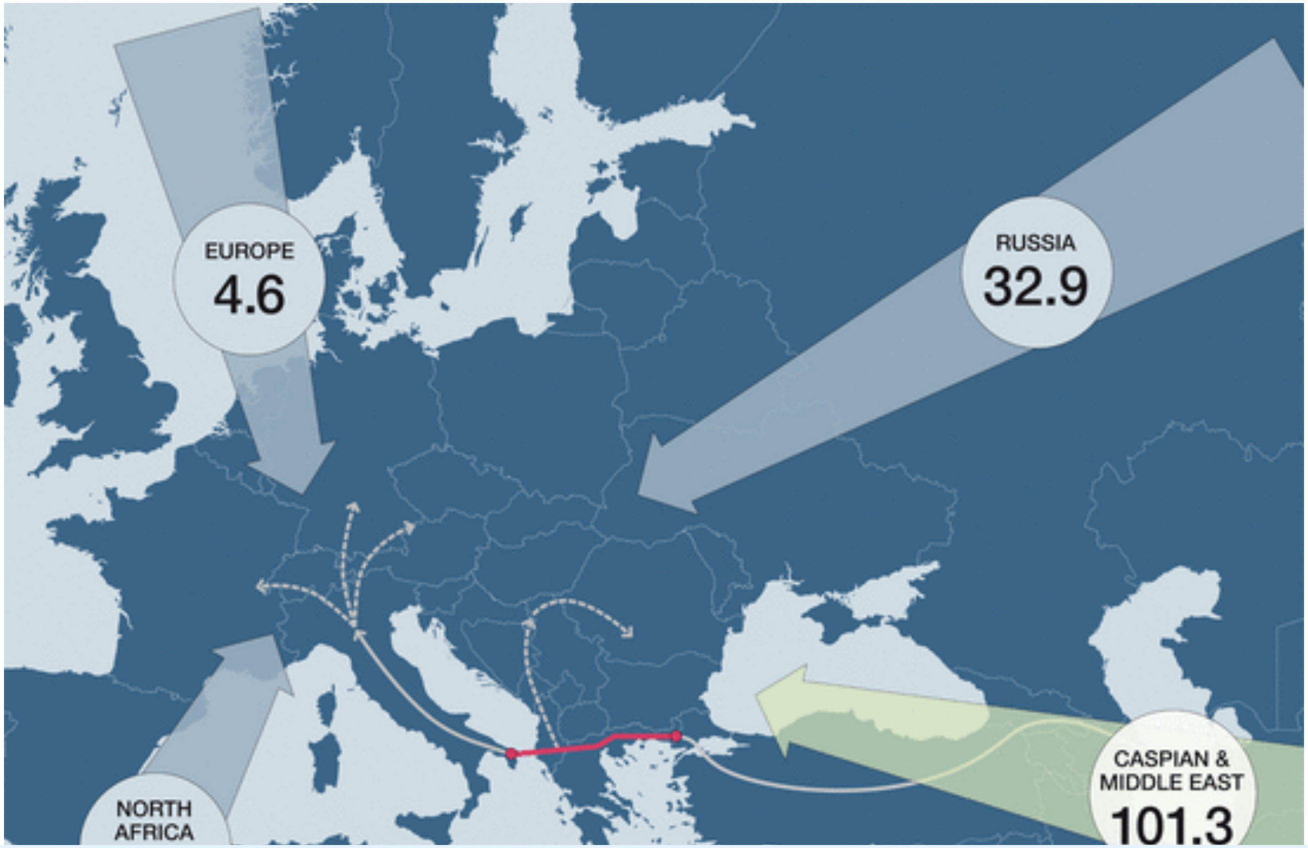
1 kW_{el}
2.5 kW_{th}

OPEL

Already available and affordable!
139 g CO_2/km (gasoline car: 169 g CO_2/km)

Combined cycle power plant η_{el} up to 60%

Distribution via natural gas grid



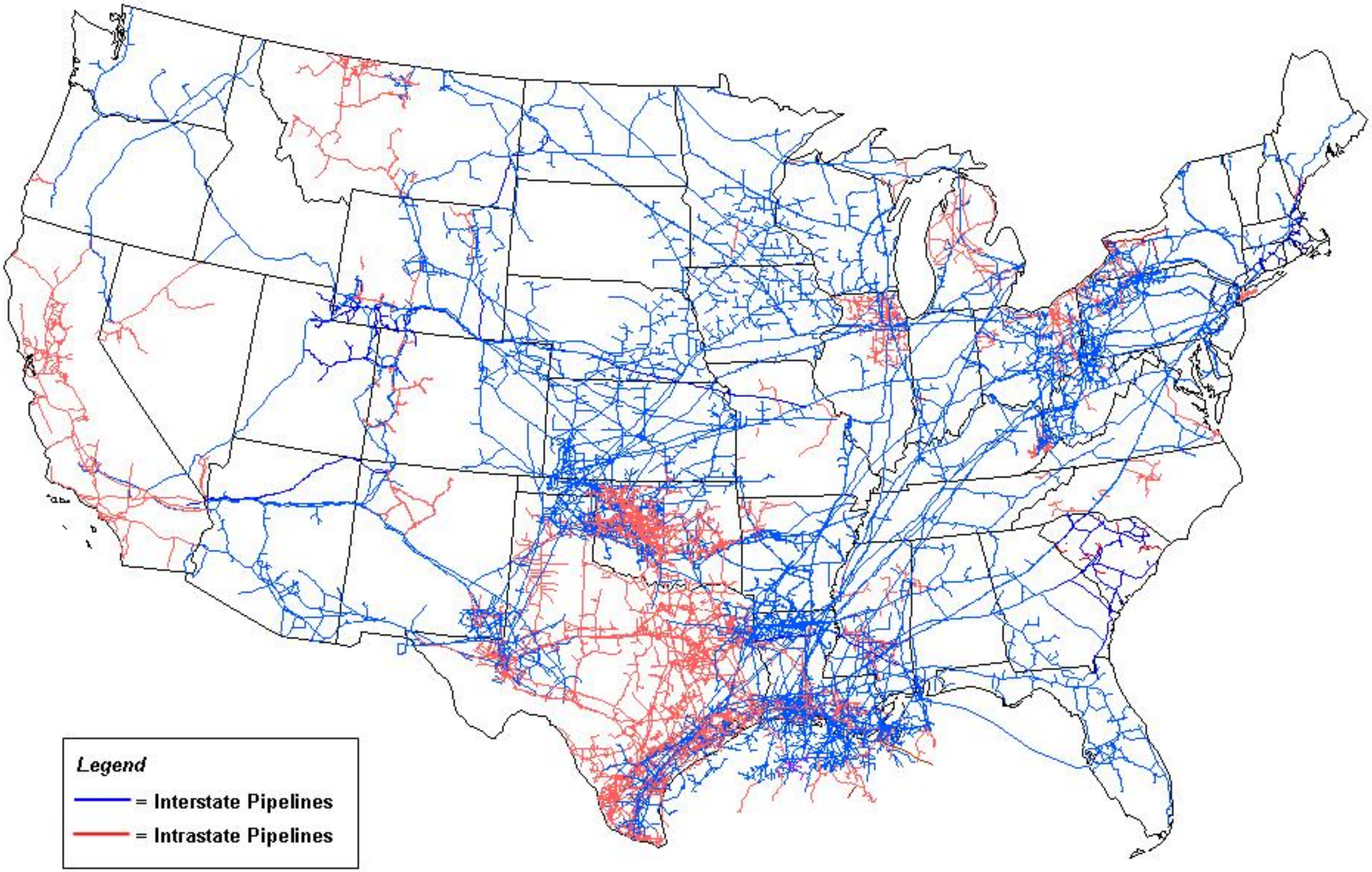
[in trillion m^3]

Source: BP World Energy Statistical Review 2012

→ Gas infrastructure is existing and will be extremely well developed in the near future

→ Biomethane has a big potential!!!

Distribution via natural gas grid in USA



Source: Energy Information Administration, Office of Oil & Gas, Natural Gas Division, Gas Transportation Information System

Comparison with other technologies

Characteristic	Hydrothermal gasification	Anaerobic digestion	Conventional gasification & methanation
Feed type	Most wet types (m_{water} > 60 %)	Manure, Household residues, sewage sludge, marine algae	Wood, grass, (m_{water} < 15 %)
Thermal efficiency (biomass to SNG)	62-71 % (Manure, wood)	25-35 %(< 8 wt % DM manure)	54-58 % (absolutely dry wood)
Residence time	< 30 min	20-22 days	< 10 min
Technological readiness	R&D	Very good (commercially available)	Good (PDU 1 MW_{SNG} in Güssing 2008)

A. G Haiduc et al., J Appl Phycol, 2009, **21**, 529-541

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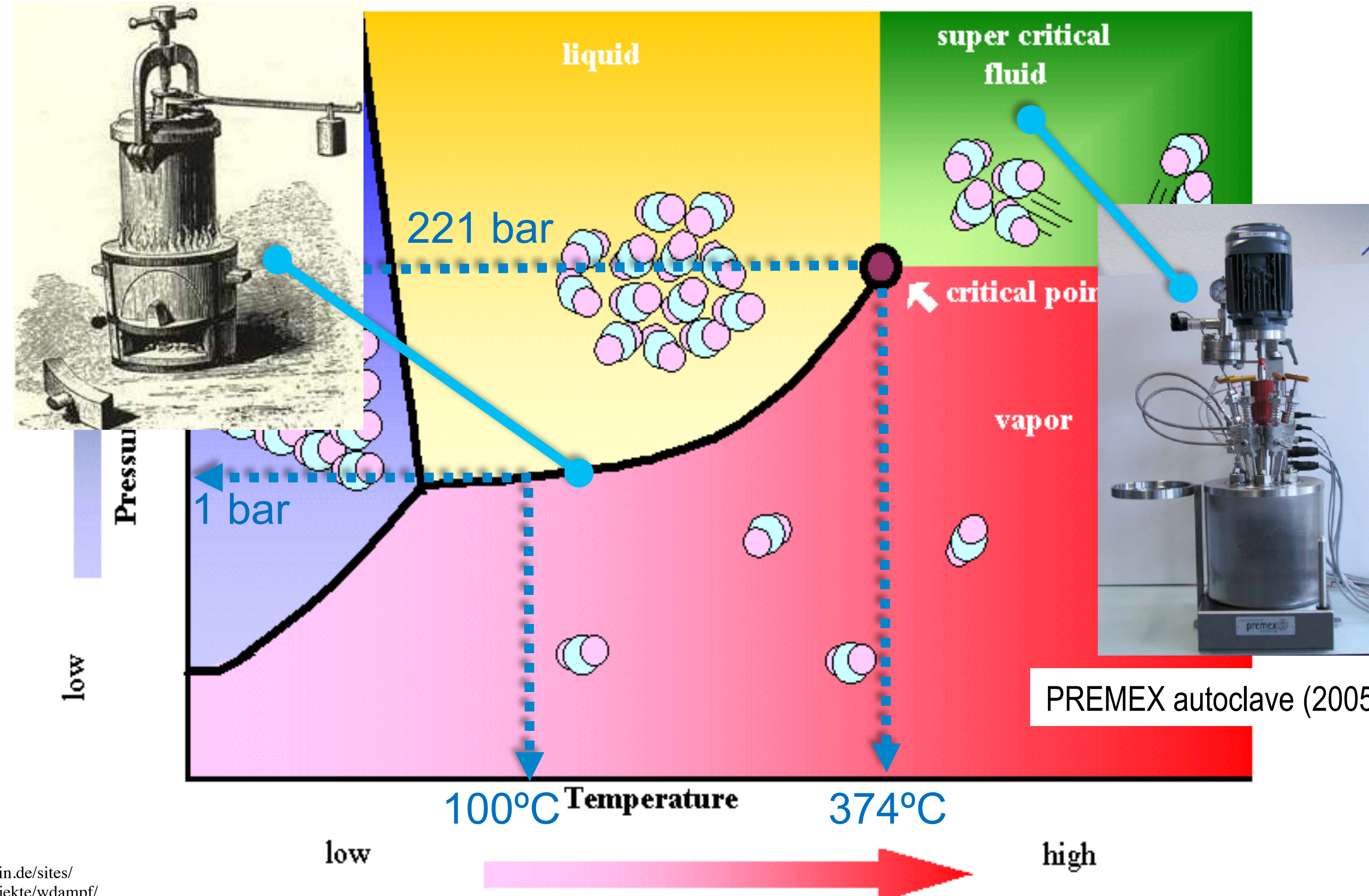
The super pressure cooker: avoiding evaporation

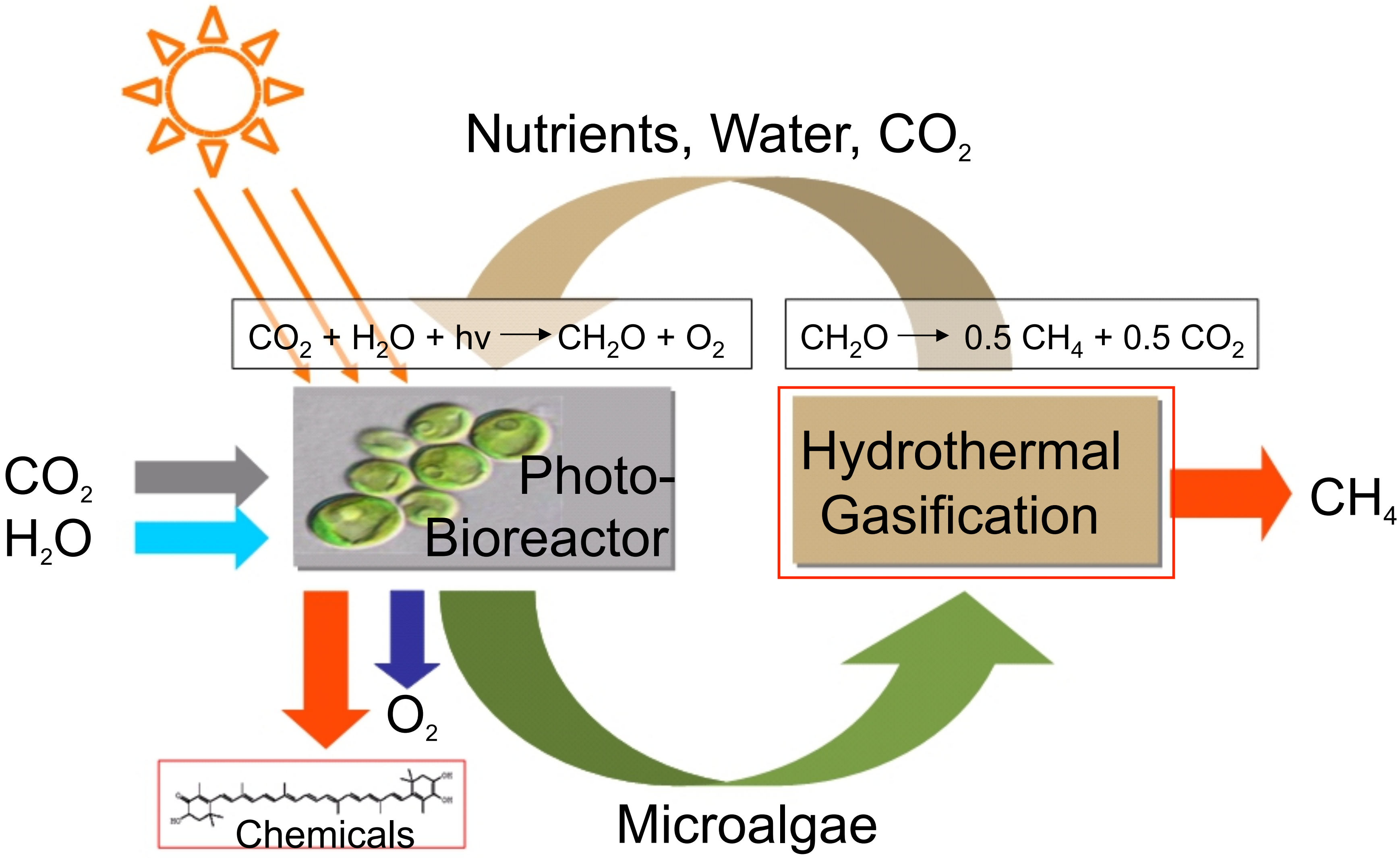
Pressure cooker by Denis Papin (1679)



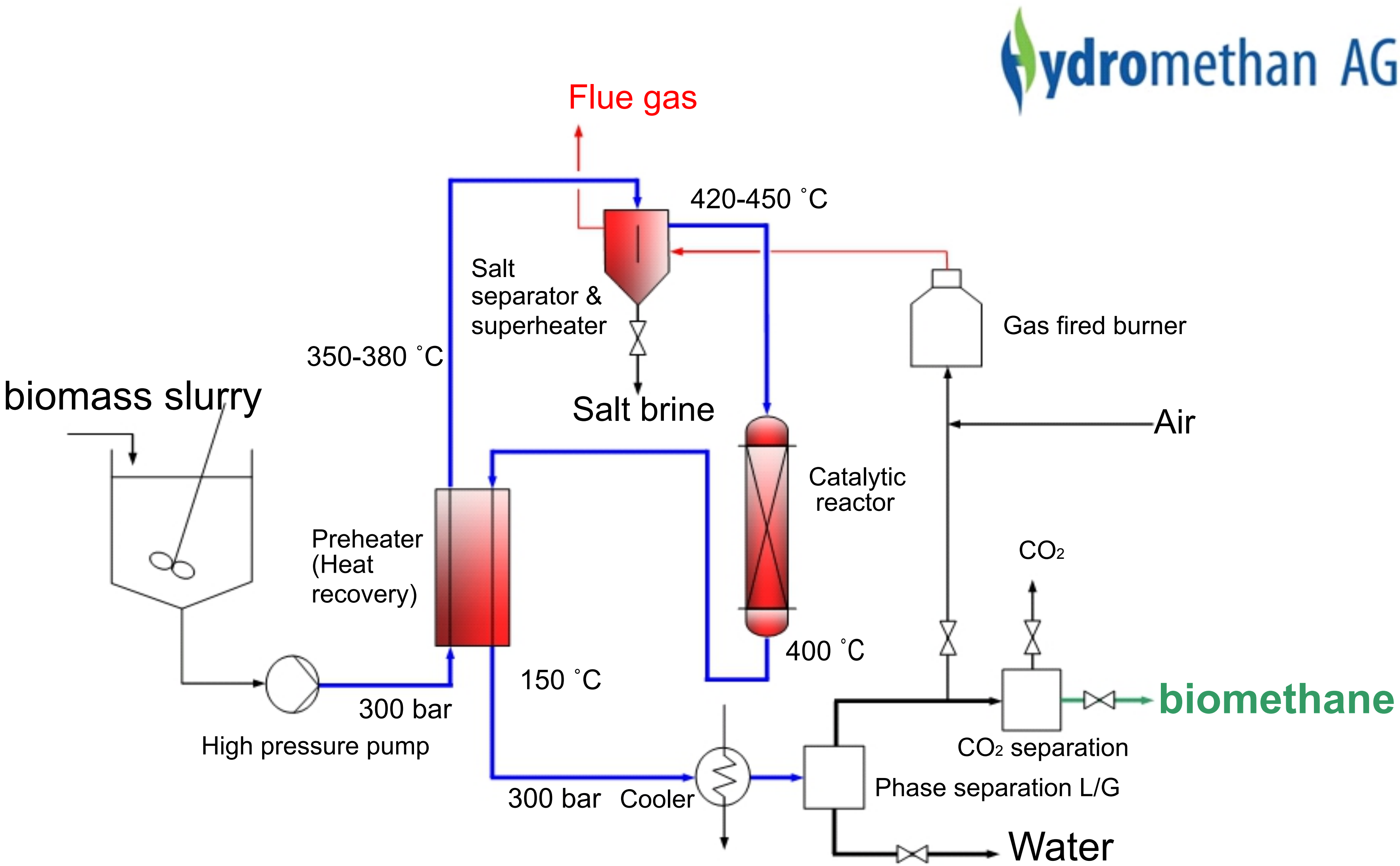
http://staugustin.de/sites/
staugustin/projekte/wdampf/
apapkoch.htm

http://www.che.tohoku.ac.jp/

SunCHem process: closed-loop system



Hydrothermal gasification process at PSI



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Hydrothermal Gasification Process at PSI

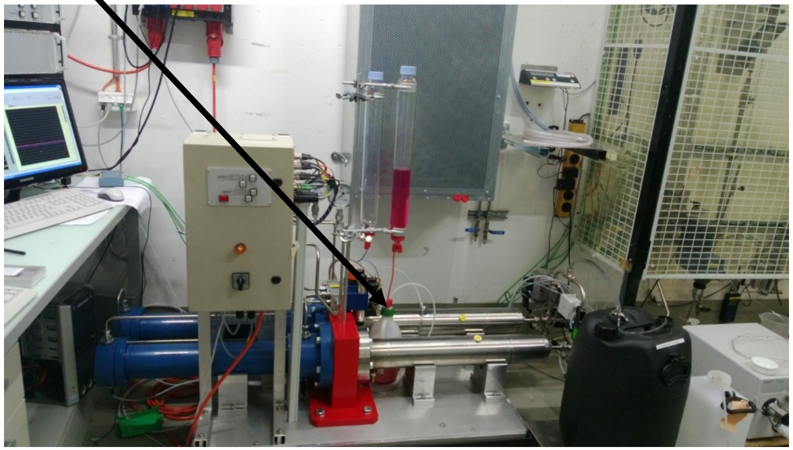
energieschweiz axpo VELUX STIFTUNG ccem.ch

Catalytic reactor

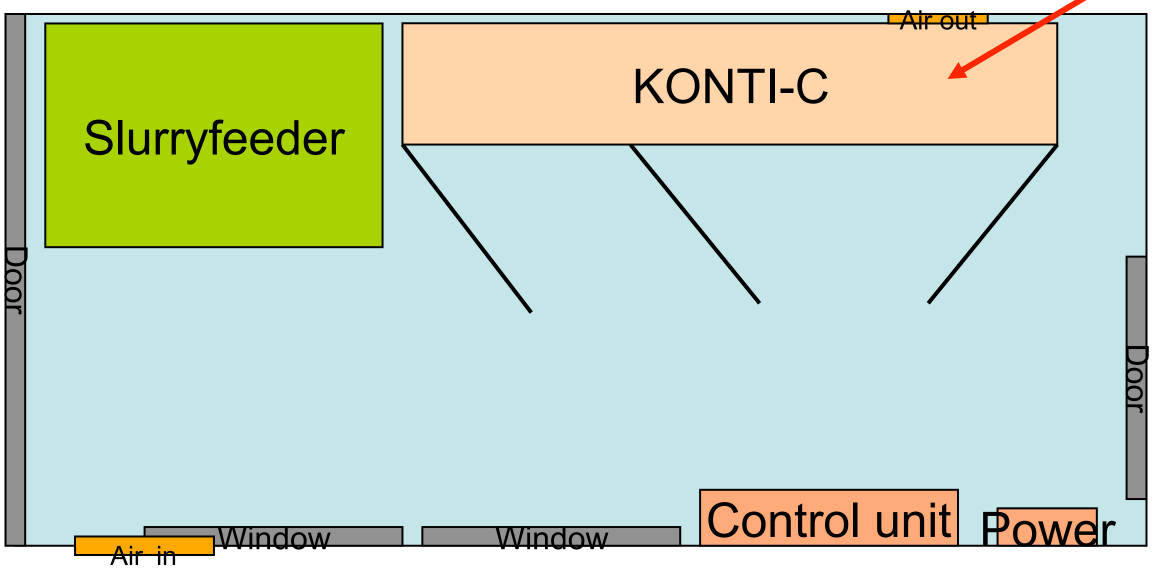
Slurry feeder

Salt separator

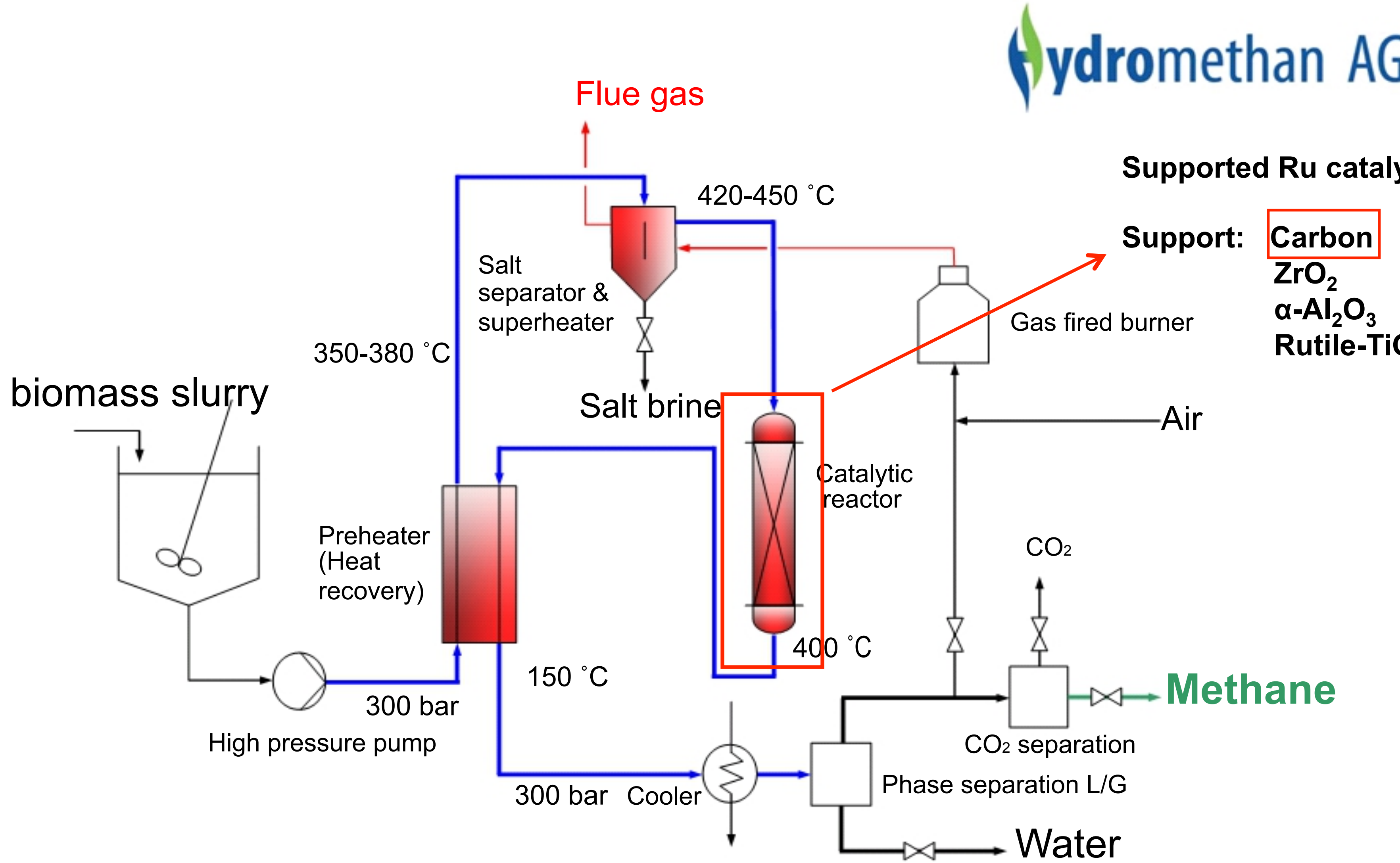
Preheater



Container KONTI-C



Hydrothermal Gasification Process at PSI

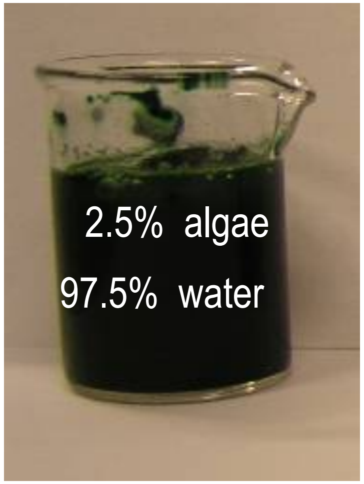


Supported Ru catalysts:

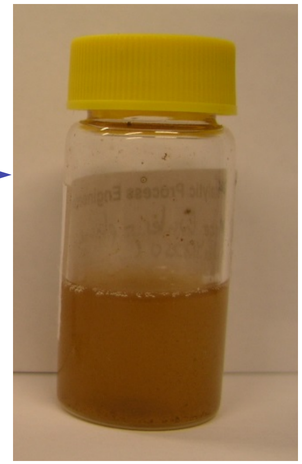
Support: **Carbon**
ZrO_2
α-Al_2O_3
Rutile-TiO_2

Hydrothermal gasification of microalgae (Chlorella)

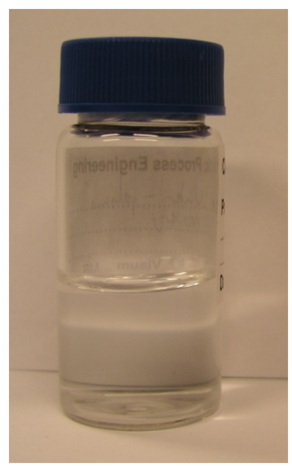
Experiment at 400 ^oC, 300 bar



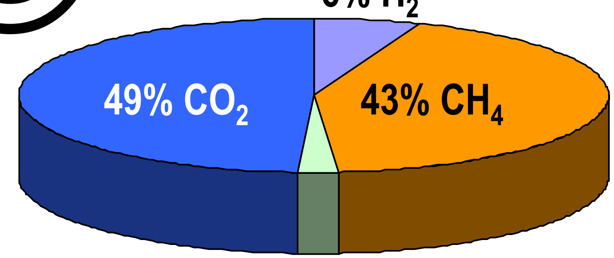
without catalyst



with catalyst



Composition of the product gas (dry basis)



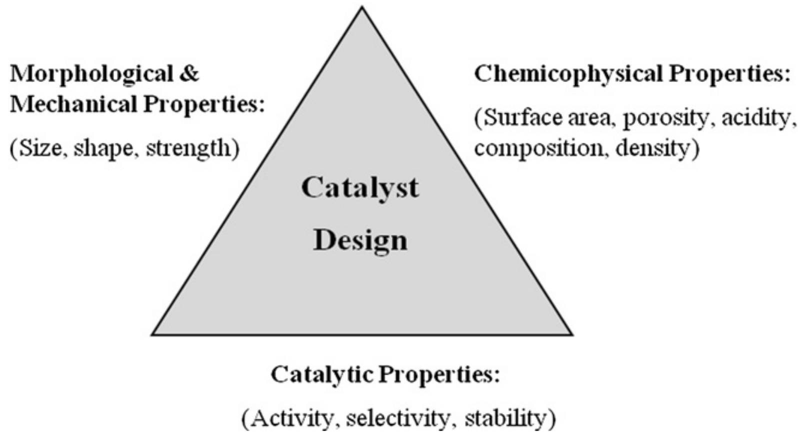
2% higher hydrocarbons (ethane, ...)

Batch reactor (54 ml)

Motivation for designing the Ru/C catalysts

« Better understanding of the relationships between catalyst formulation and structure related to its catalytic performance »

That's the key to further advance the effectiveness of the Ru/C catalysts for CSCWG!



Ref: Azadi P. et al., Review of heterogeneous cat., Hydrogen and energy, 2011, vol. 36, 9529-41

Relevant properties:

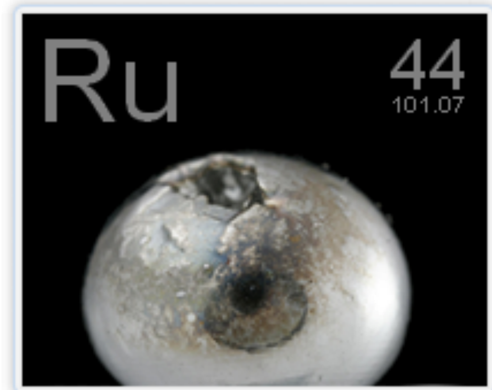
- Meso/microporous structure
- Impurities (**S**, P, Cl,…)
- Surface acidity
- Graphitization degree
- Ru dispersion
- Ru loading

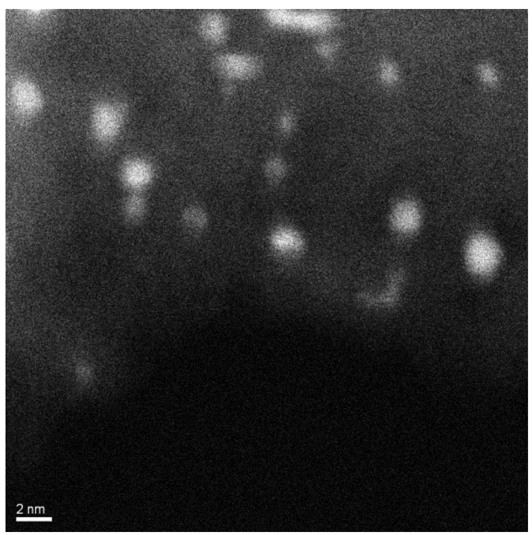
Synthesis of the Ru/C catalysts

Source: www.dampfkoenig.ch

+

Source: www.dfgoldsmith.com





$RuCl_3 \cdot xH_2O$
or $Ru(NO)(NO_3)_x(OH)_y$
by wet impregnation

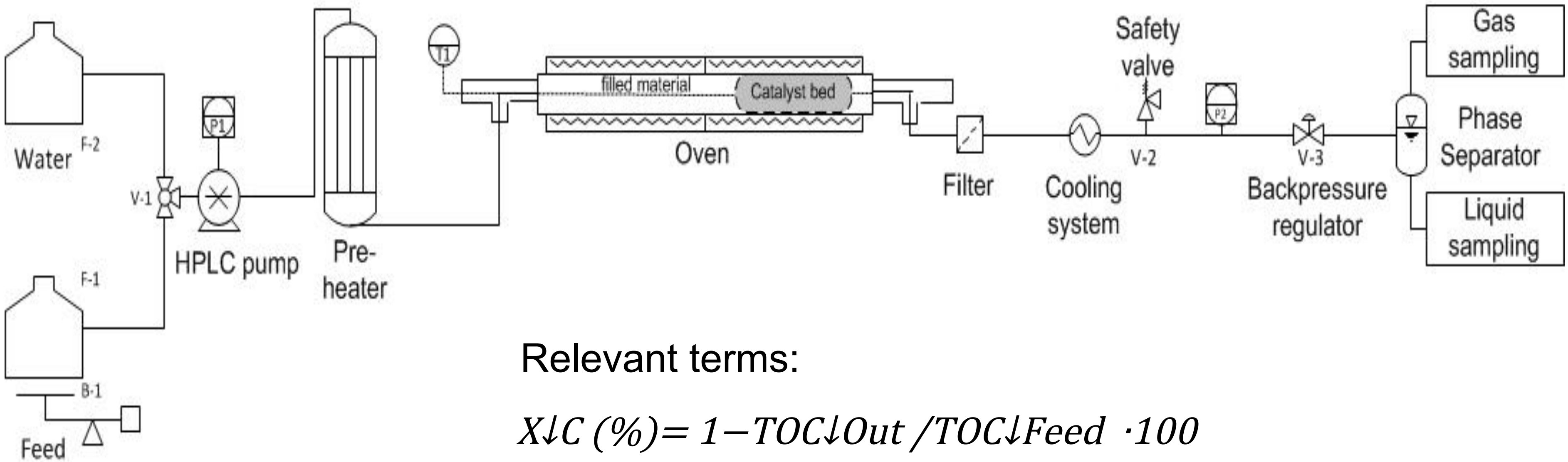
HAADF-STEM image of the 2% Ru/C

Fixed-bed PF reactor for CSCWG of model compounds

Objective

- Catalytic performances assessment of the Ru/C catalysts with 10 wt. % isopropanol

Working conditions: T = 450 ˚C, P = 300 bar, F = 3 g/min



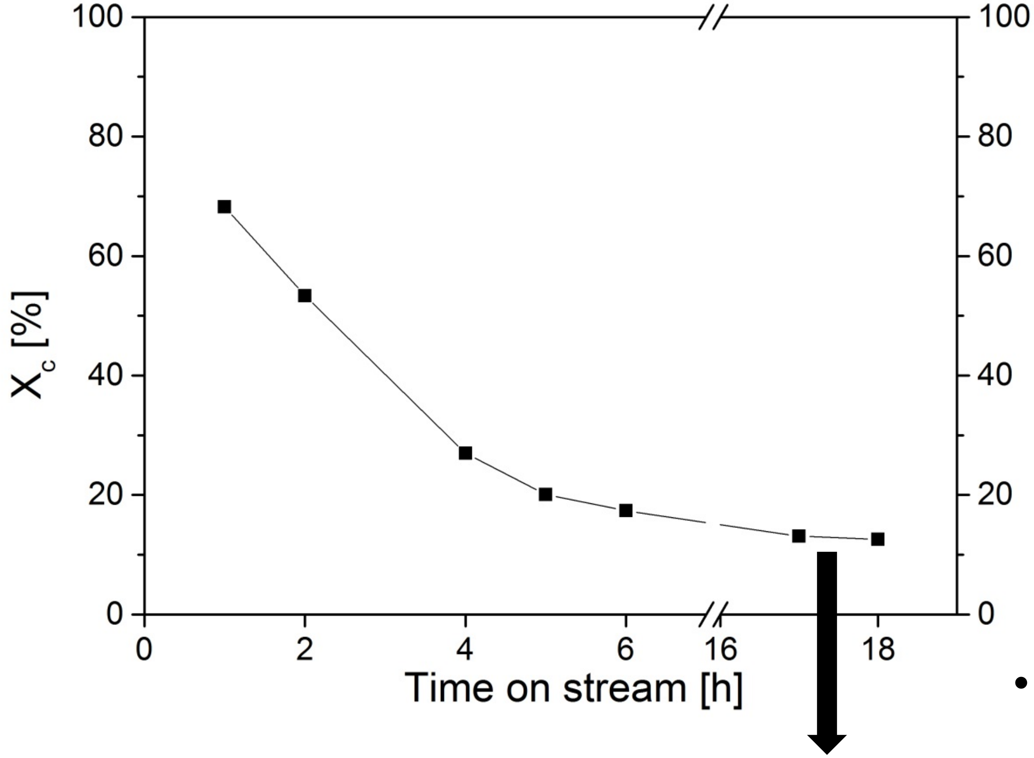
Relevant terms:

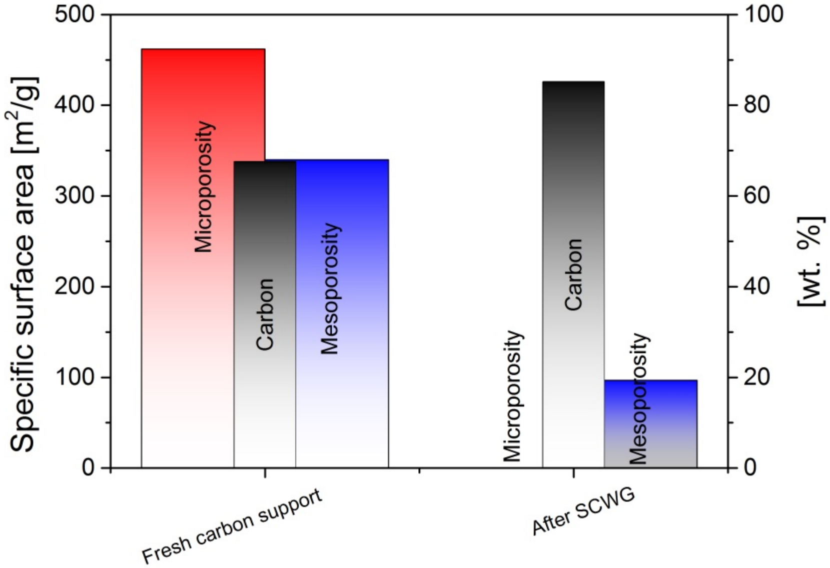
$$X_C\,(\%) = 1 - \frac{TOC_{Out}}{TOC_{Feed}} \cdot 100$$

$$GE_C\,(\%) = \frac{Total\ molC_{Gas}}{Total\ molC_{Feed}} \cdot 100$$

SCWG over the carbon support

T = 450 ˚C, P = 300 bar, 10 wt. % isopropanol

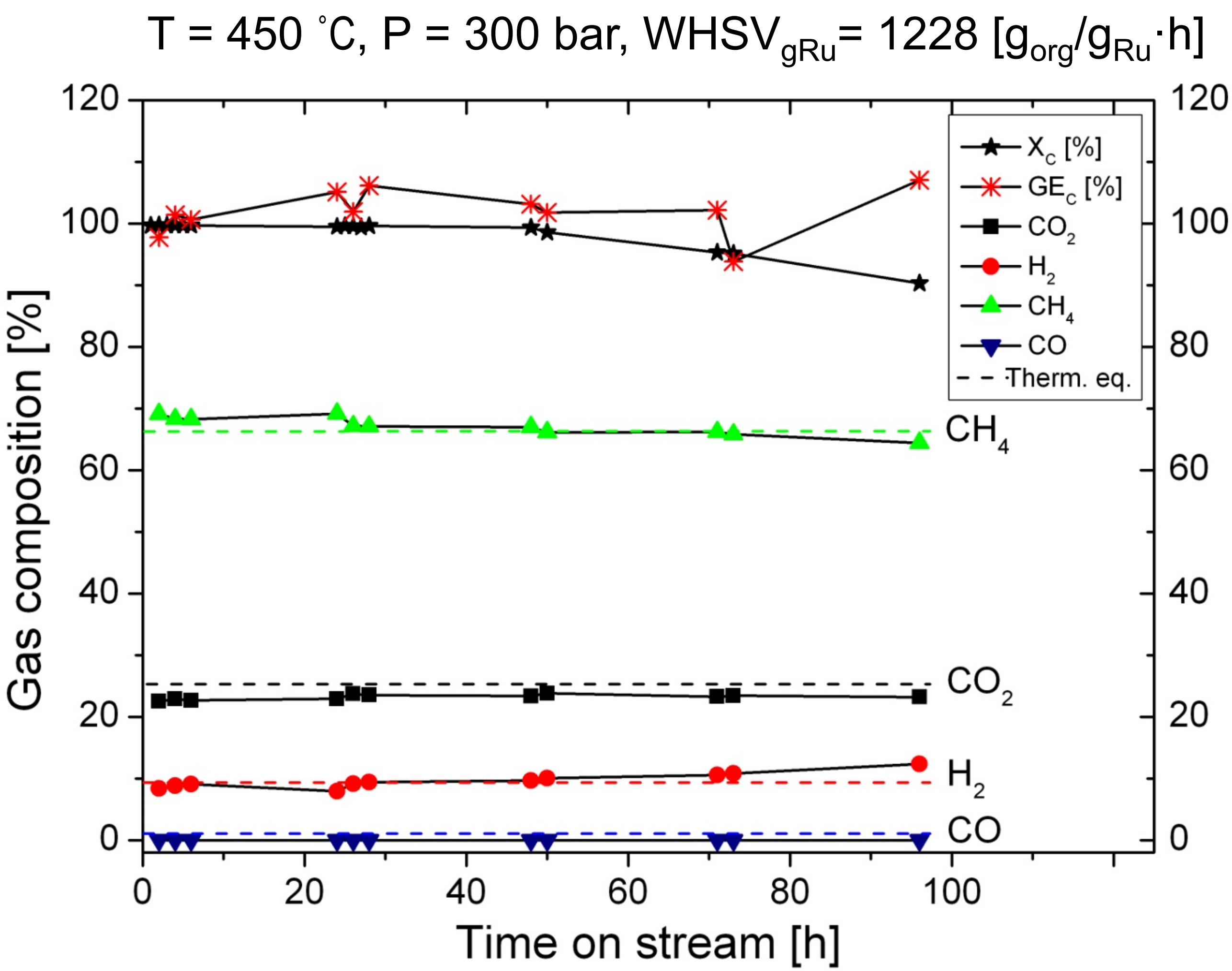




- Coke deposition during SCWG!

Time on stream [h]	X_C [%]	GE_C [%]	$R_{Coke\ dep.}$ [mmol C/min]	Gas composition [vol. %]				
				CH_4	CO_2	H_2	CO	C_3H_8
18	11	3.6	1.1	3.3	0.5	96	0.2	5

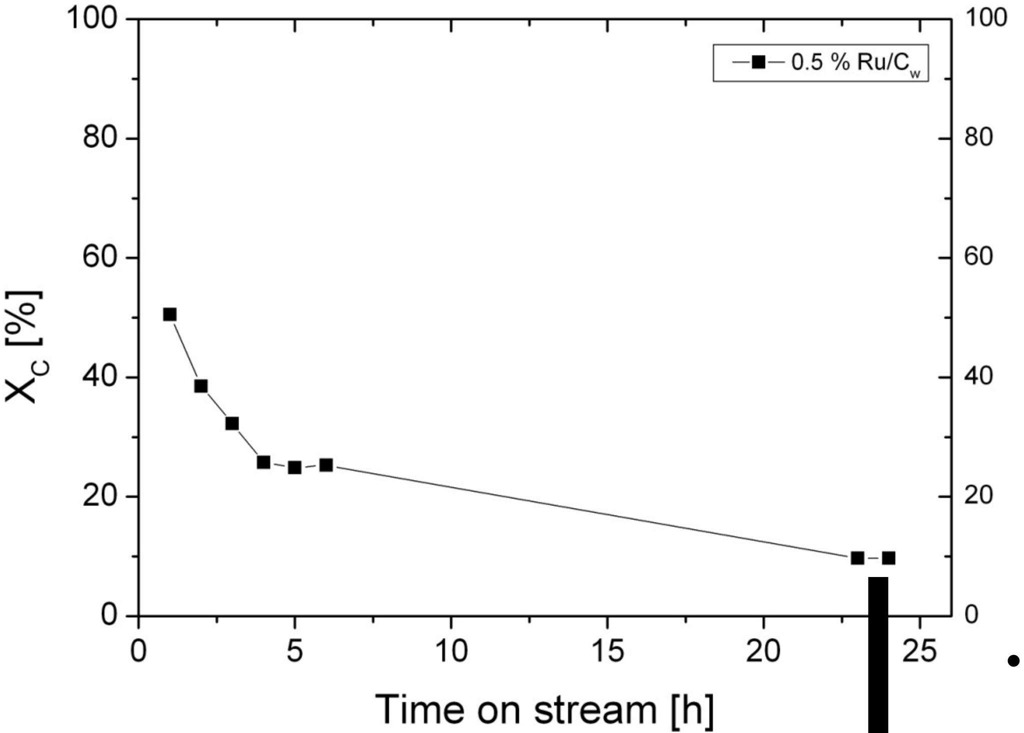
CSCWG of 10 wt.% isopropanol over the 2% Ru/C

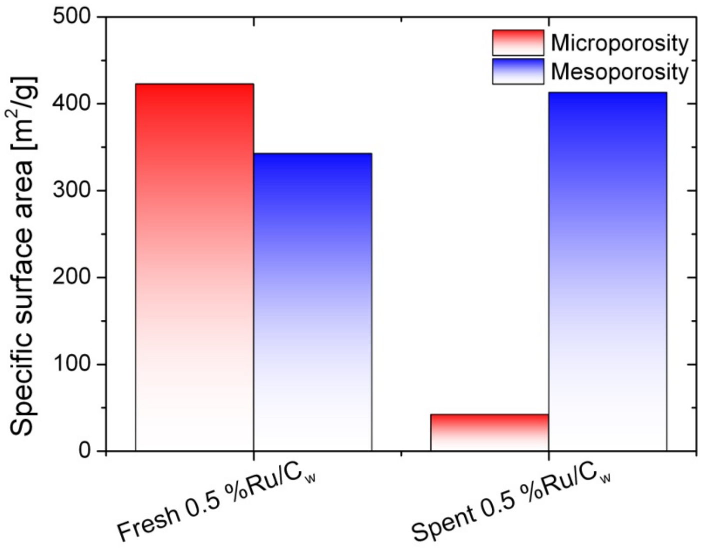


- Good catalytic performances over 96 hours with gas composition close to thermodynamic chemical equilibrium

Stability of the 0.5% Ru/C_w

T = 450 °C, P = 300 bar, $WHSV_{gRu}$= 5202 [$g_{org}/g_{Ru}\cdot h$]



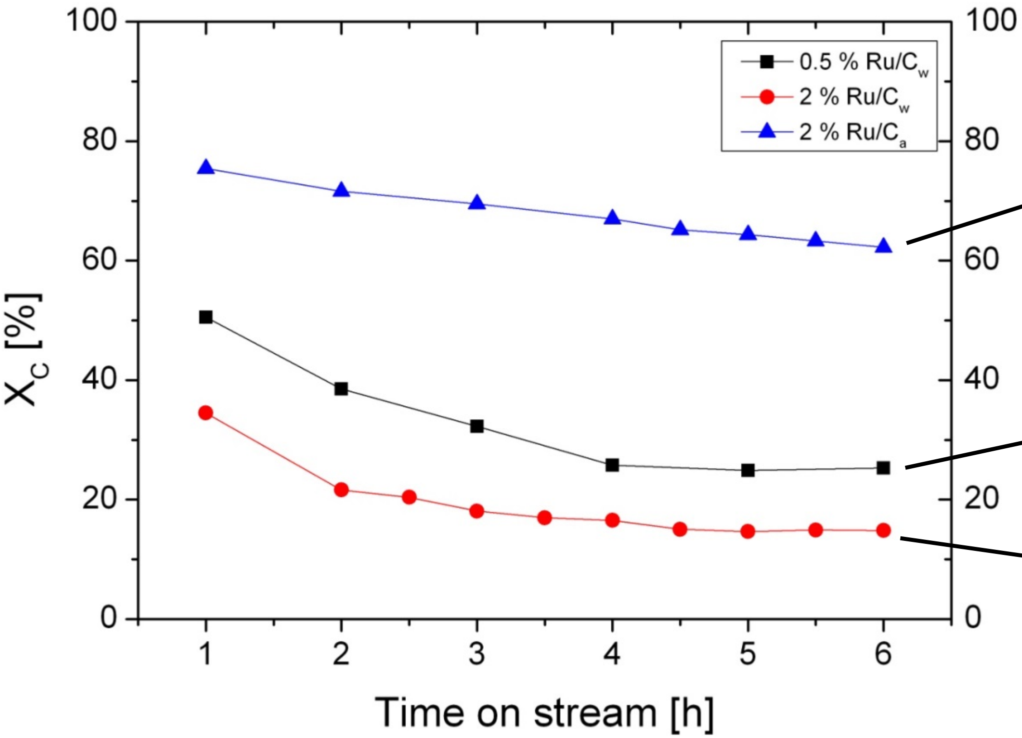


- Catalyst deactivation by coke deposits!

X_C	GE_C	$R_{Coke\ dep.}$	Gas composition [vol. %]				
[%]	[%]	[mmol C/min]	CH_4	CO_2	H_2	CO	C_3H_8
9.7	3.4	0.9	3.2	0.6	96	0.2	3.7

Effect of the Ru dispersion & solvent (water vs acetone)

T = 450 ˚C, P = 300 bar, $WHSV_{gRu}$= 5202 [$g_{org}/g_{Ru}\cdot h$]



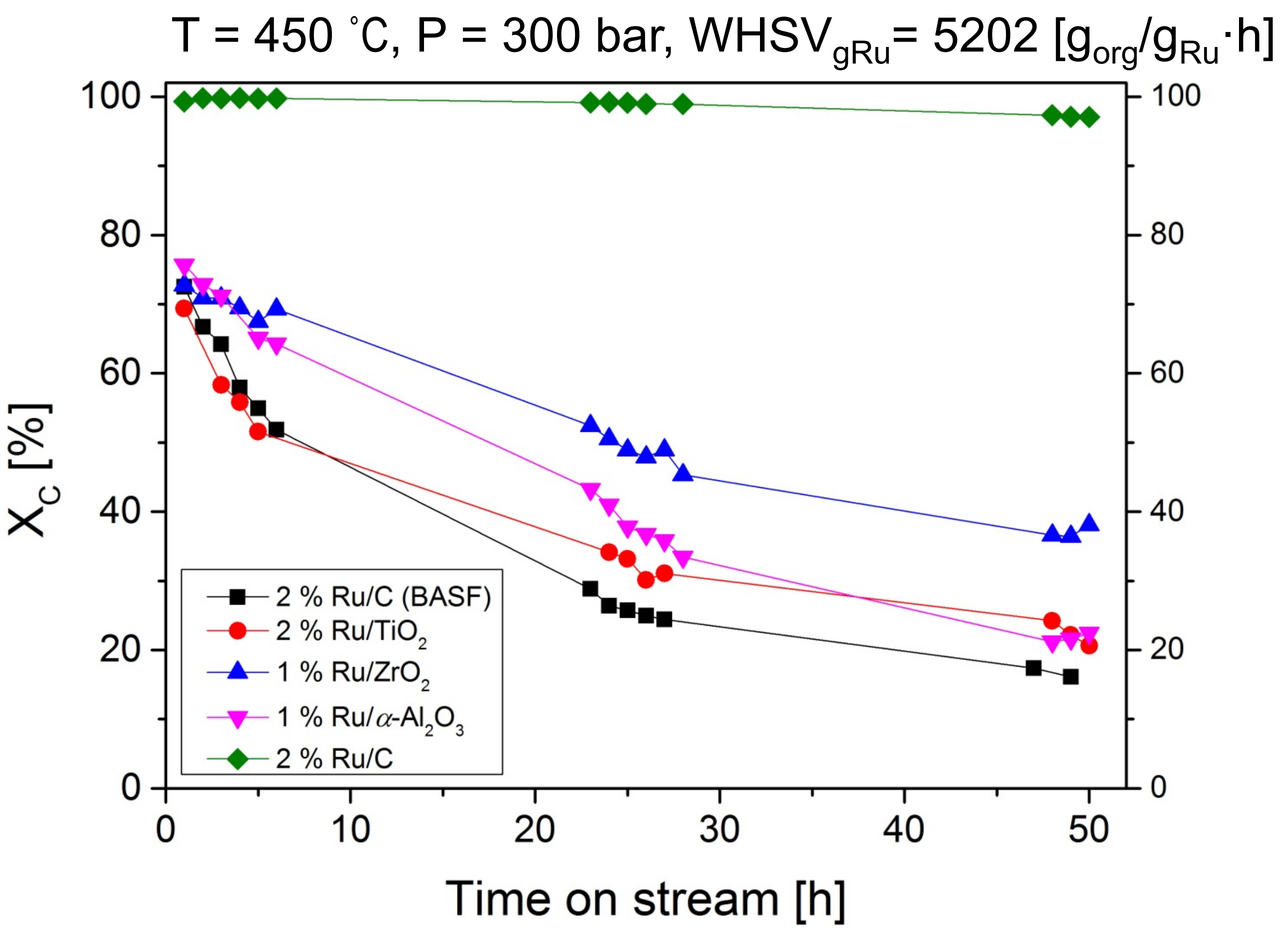
D_{CO} (11 %), d_{STEM} = 3.1 nm ±0.6

D_{CO} (12 %), d_{STEM} = 2.9 nm ±0.5

D_{CO} (8 %), d_{STEM} = 7 nm ±1.3

- High Ru dispersion (smaller Ru NPs) lead to a better activity
- The use of acetone improved significantly the activity (higher Ru dispersion and a lower concentration of residual Cl^- coming from $RuCl_3\cdot xH_2O$)

Carbon vs metal oxide supports



- The Ru/C catalyst is the most suitable catalyst
- Better catalytic performances than the 2% Ru/C (BASF) (use of $Ru(NO)(NO_3)_x(OH)_y$)

Conclusion and perspectives

- Hydrothermal gasification process is a promising technology for biomethane production

- Remaining challenges are:

- Efficient salt separation
- Ensure stable working operations (plugging due to tar formation)
- Sulfur removal by S-adsorbent agent
- Develop robust catalysts for CSCWG (regarding coking, sulfur,…)