



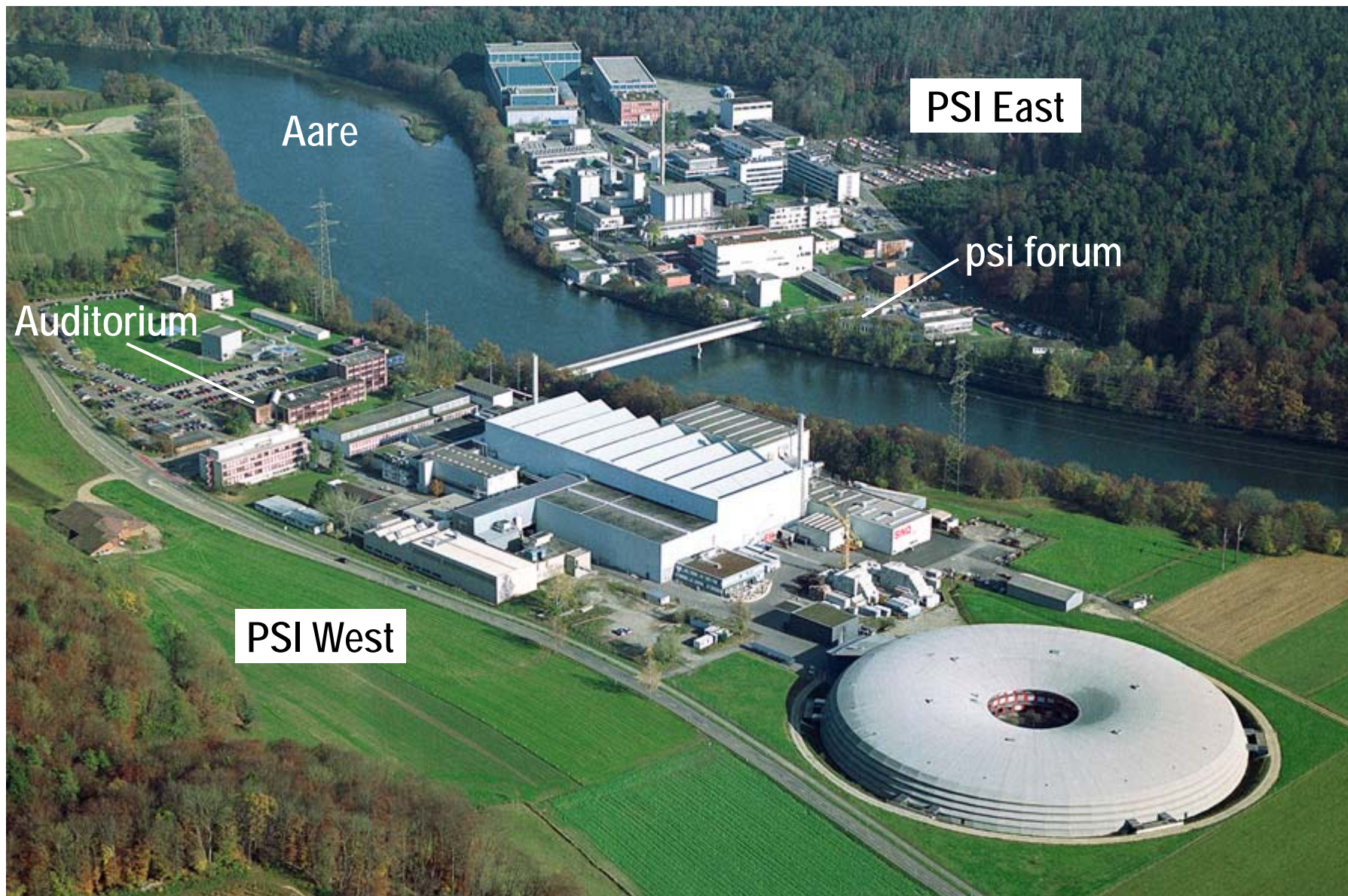
Wir schaffen Wissen – heute für morgen

Paul Scherrer Institut

Frédéric Vogel

**Catalytic hydrothermal conversion of biomass to
methane**

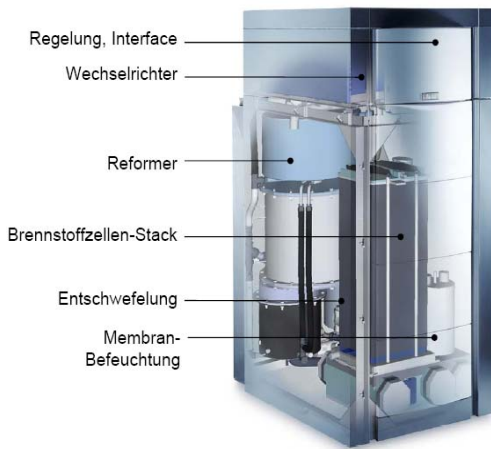
1. PSI's biofuel strategy – why methane?
2. Biomass processing and catalysis in supercritical water
3. PSI's catalytic hydrothermal SNG process:
 - main results
 - status
 - outlook



...for centralized, decentralized, and mobile applications



Already available and affordable today!
138 g CO₂/km (Gasoline: 169 g CO₂/km)



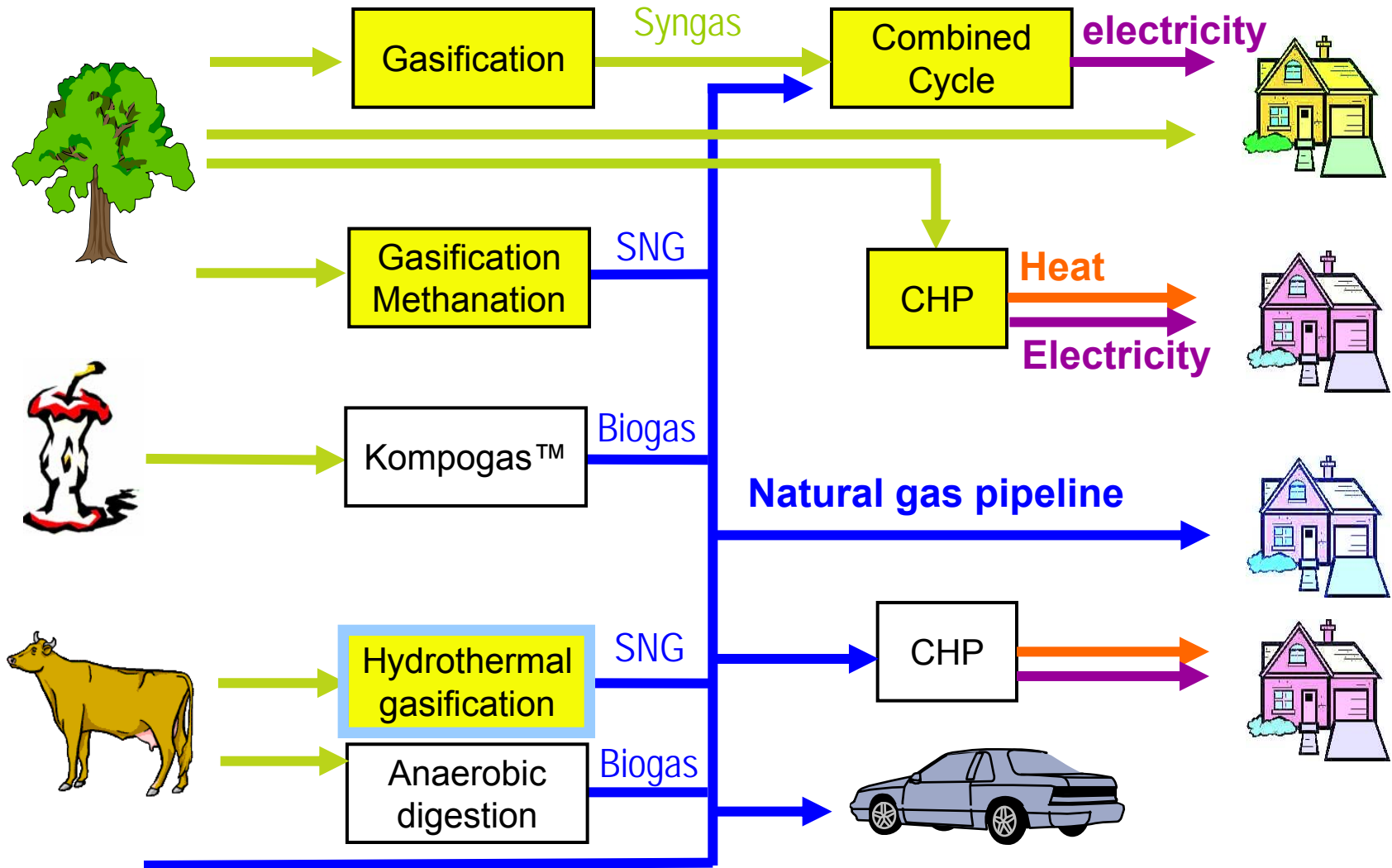
1-4.6 kW_{el}
1.5-7 kW_{th}



1 kW_{el}
2.5 kW_{th}



Integration of biomass into existing grids



1 CHF = 0.90 USD
= 0.74 EUR
= 420 CLP

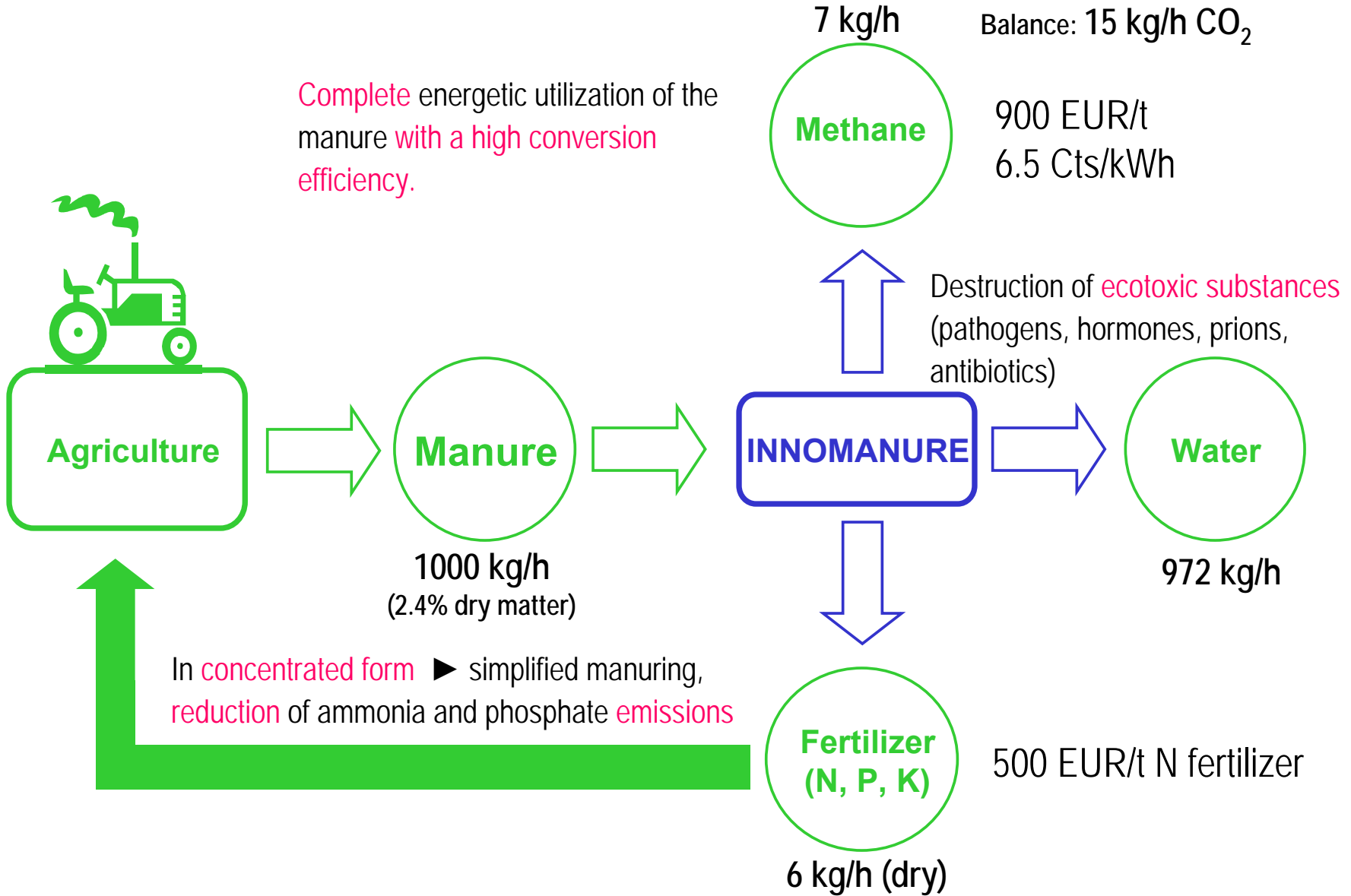
CHF per ton (dry matter)*

	Bezeichnung	Kategorie	Kosten in CHF/t					
			2003		2025		2040	
			Min	Max	Min	Max	Min	Max
Clean wood Energy crops	Waldholz, Feldgehölze, Hecken	a	80	510	80	350	80	400
	Energiepflanzen, Ackerkulturen	b	200	220	130	150	130	180
	Kartoffeln	b	0	20	20	60	40	80
	Wiesland	c	136	350	150	200	180	250
	Stroh	d	100	150	85	130	70	110
Liquid manure	Gülle	d	0	0	0	0	0	0
	Strukturreiche Biomasse von Uferböschungen, Naturschutzflächen	e	-150	-50	-100	-20	-50	0
	Strukturreiche Biomasse von Verkehrsflächen	f	-150	-50	-100	-20	-50	0
	Altholz	g	-40	0	20	40	20	40
	Restholz	h	-50	0	0	100	100	150
Residential & industrial biowaste	Abfälle aus Industrie, Haushalt und Gewerbe, mit Hygienierisiko	i	-200	-100	-200	-100	-200	-100
	Abfälle aus Industrie, Haushalt und Gewerbe, risikoarm	i	-100	-30	-70	-10	-40	0

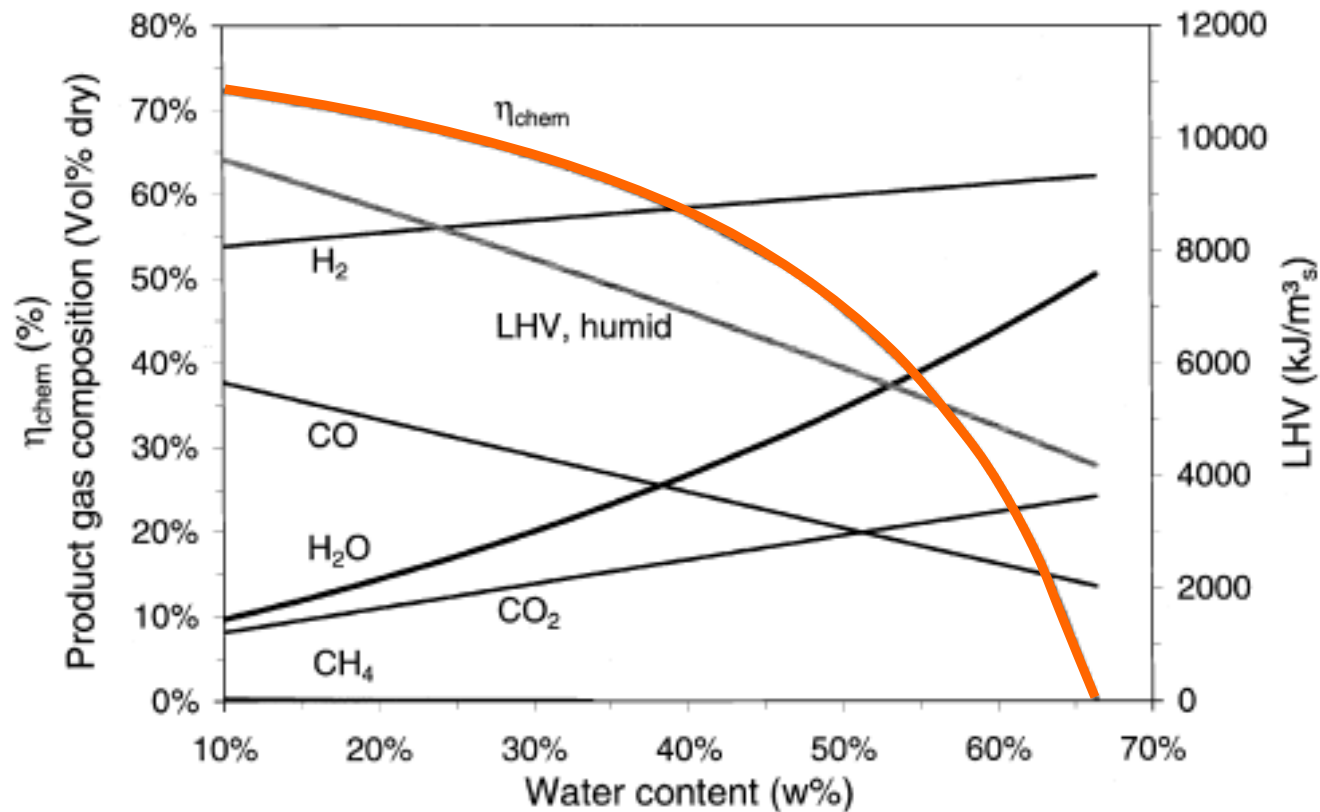
Source: Oetli et al., Bundesamt für Energie, Switzerland, 2004

*includes harvesting costs but no transportation costs

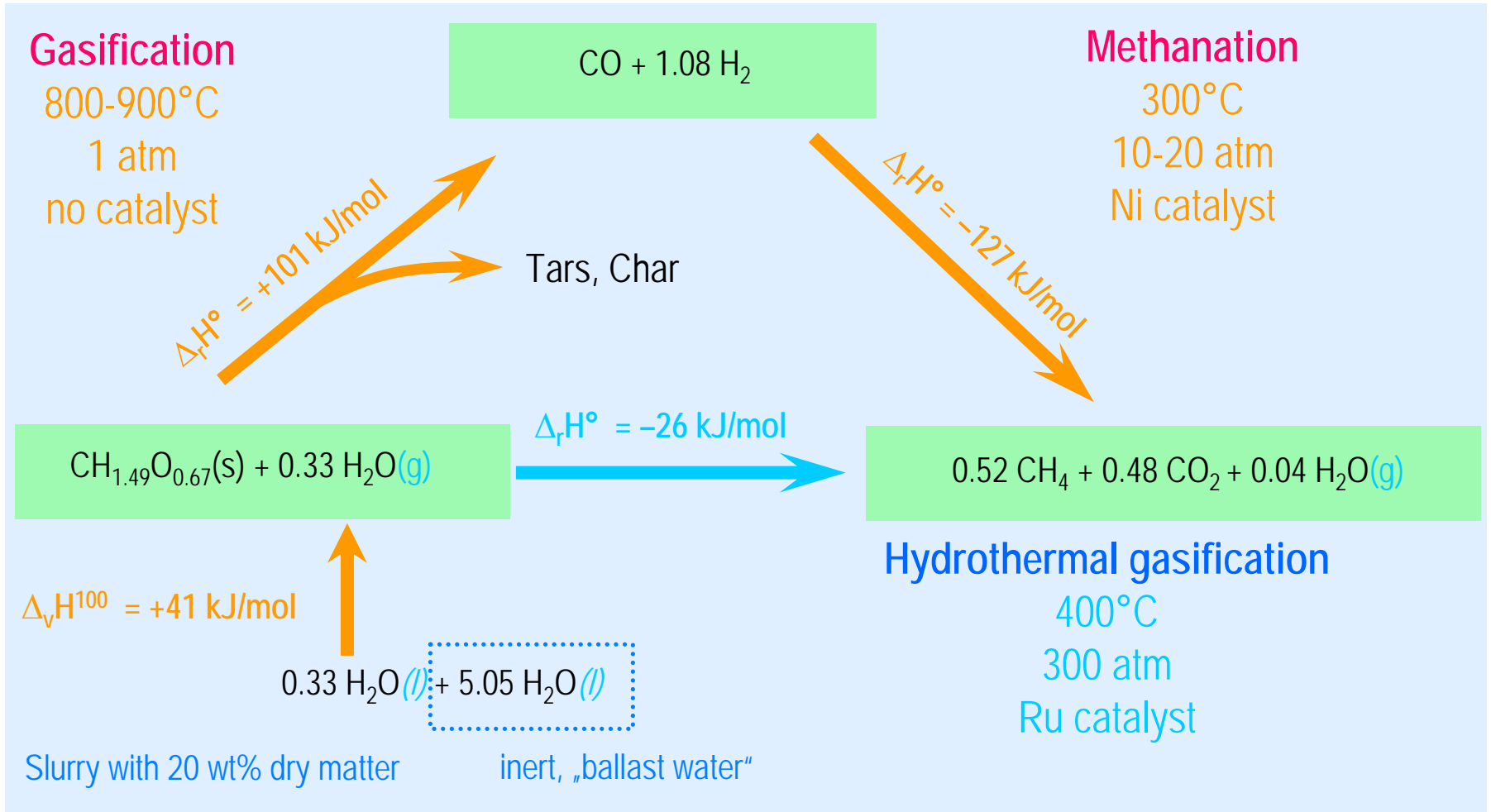
Concept for complete manure utilization



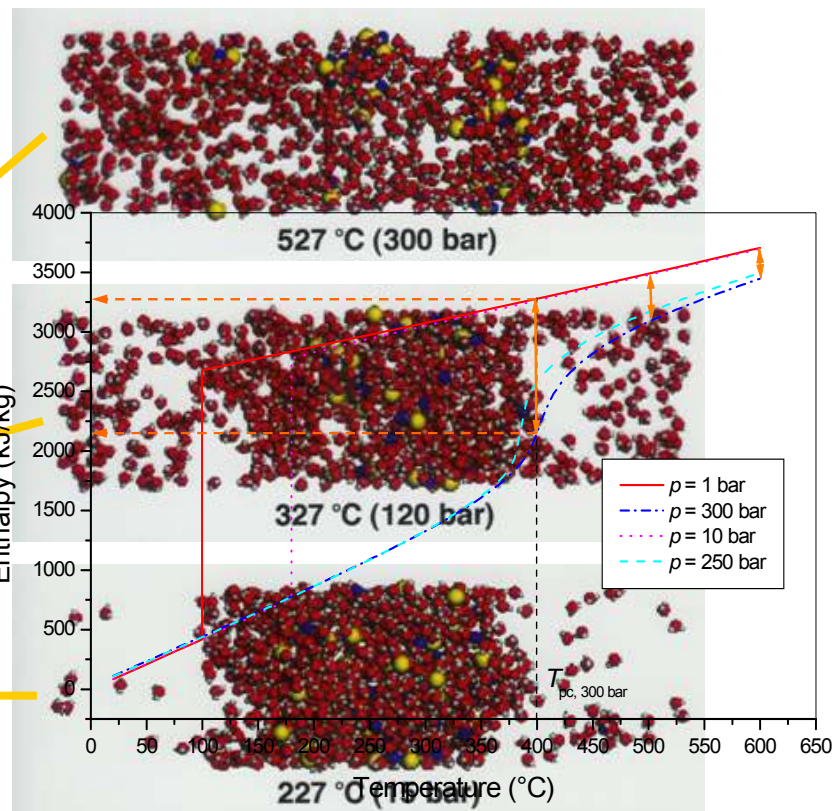
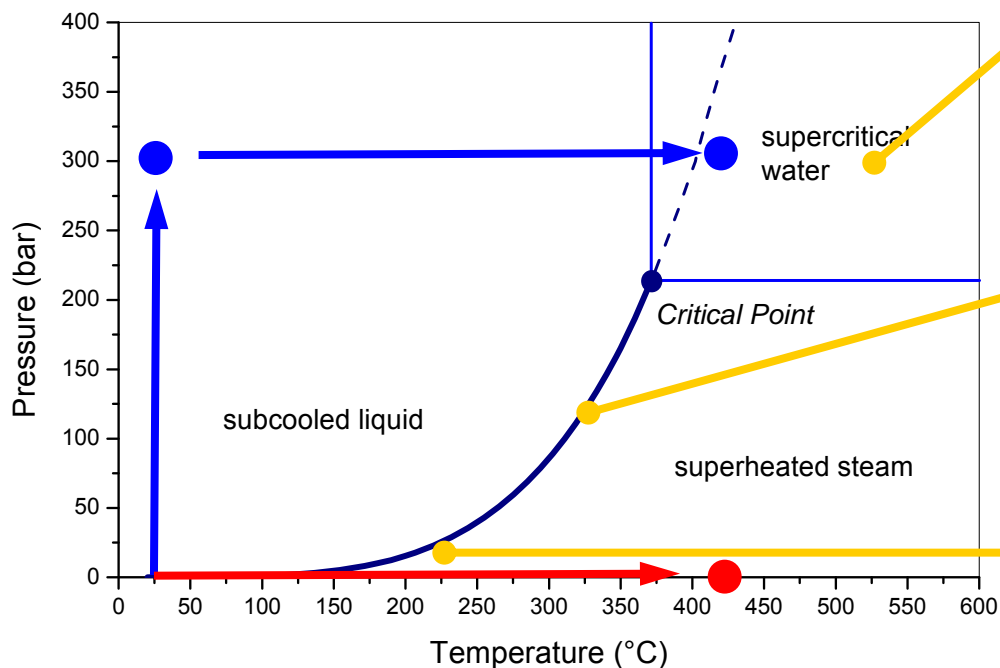
Atmospheric gasification: Process efficiency vs. water content



G. Schuster, G. Löffler, K. Weigl, H. Hofbauer, *Bioresource Technology* 2001, **77**, 71-79

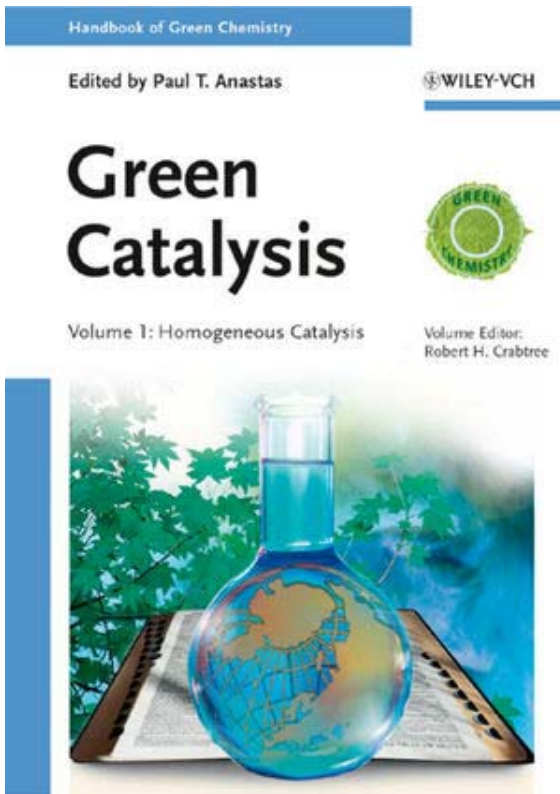


„Hydrothermal“ refers to conversions in pressurized water (200-400 bar) at temperatures of ca. 250-600°C.

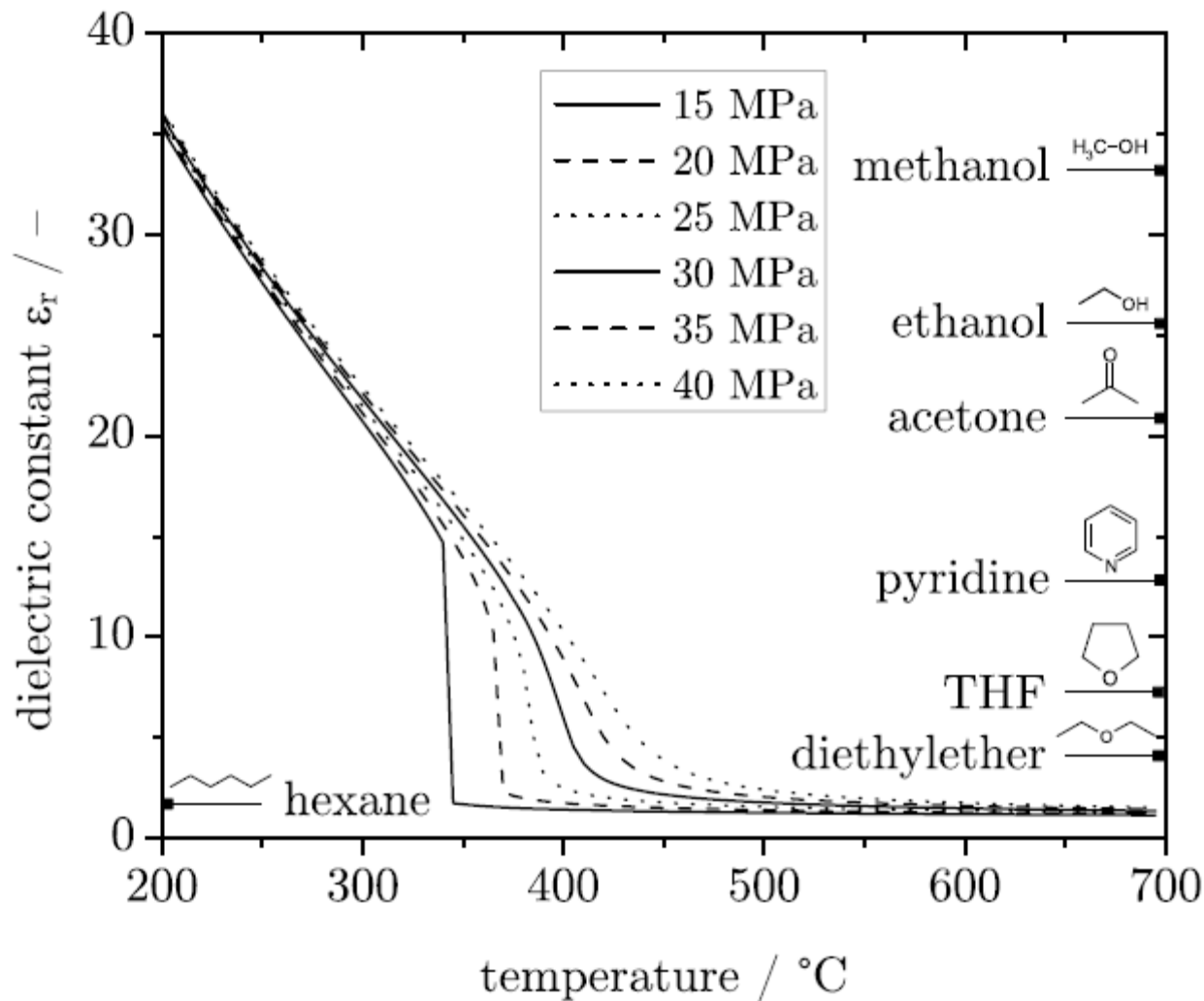


Molecular Dynamics simulations of dissolved NaCl

Reagan, M. *et al*, J. Phys. Chem. B 103 (37), (1999)



Volume 2: Heterogeneous Catalysis
WILEY-VCH, 2009



M. H. Waldner, PhD thesis, ETHZ, 2007

- Can we completely gasify the organic fraction of (wet) biomass into a methane-rich gas in supercritical water (= Supercritical Water Gasification, SCWG)?



⇒ "easy" part

...and simultaneously recover the nutrients?

⇒ difficult part!

The catalyst is the key!

Gasification of wood sawdust in an autoclave

400°C, ca. 30 MPa, $\tau = 98$ min.

No catalyst

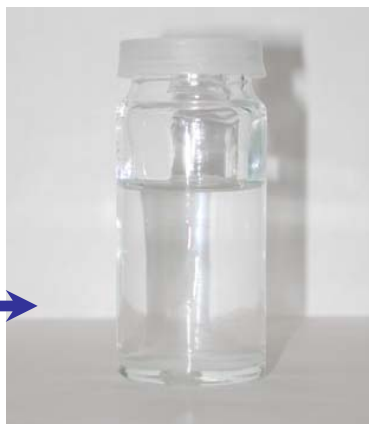


Carbon gasification: 21%
Yield: 0.02 g CH₄/g wood_{daf}

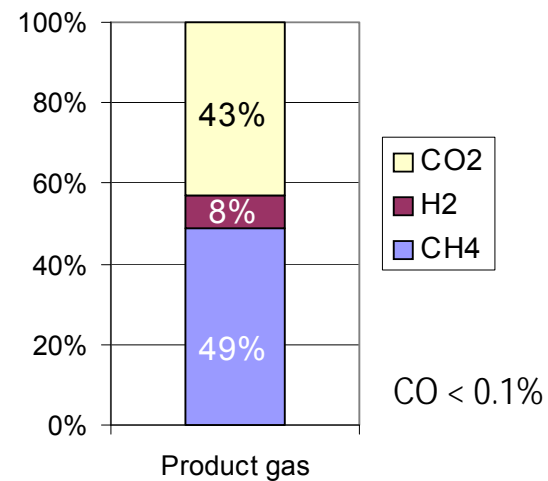
Excessive **tar** and **char** formation and only modest gasification.

10% wood in water
(TOC: 49 g/L)

Raney Ni[®]



Carbon gasification: >99%
Yield: 0.33 g CH₄/g wood_{daf}



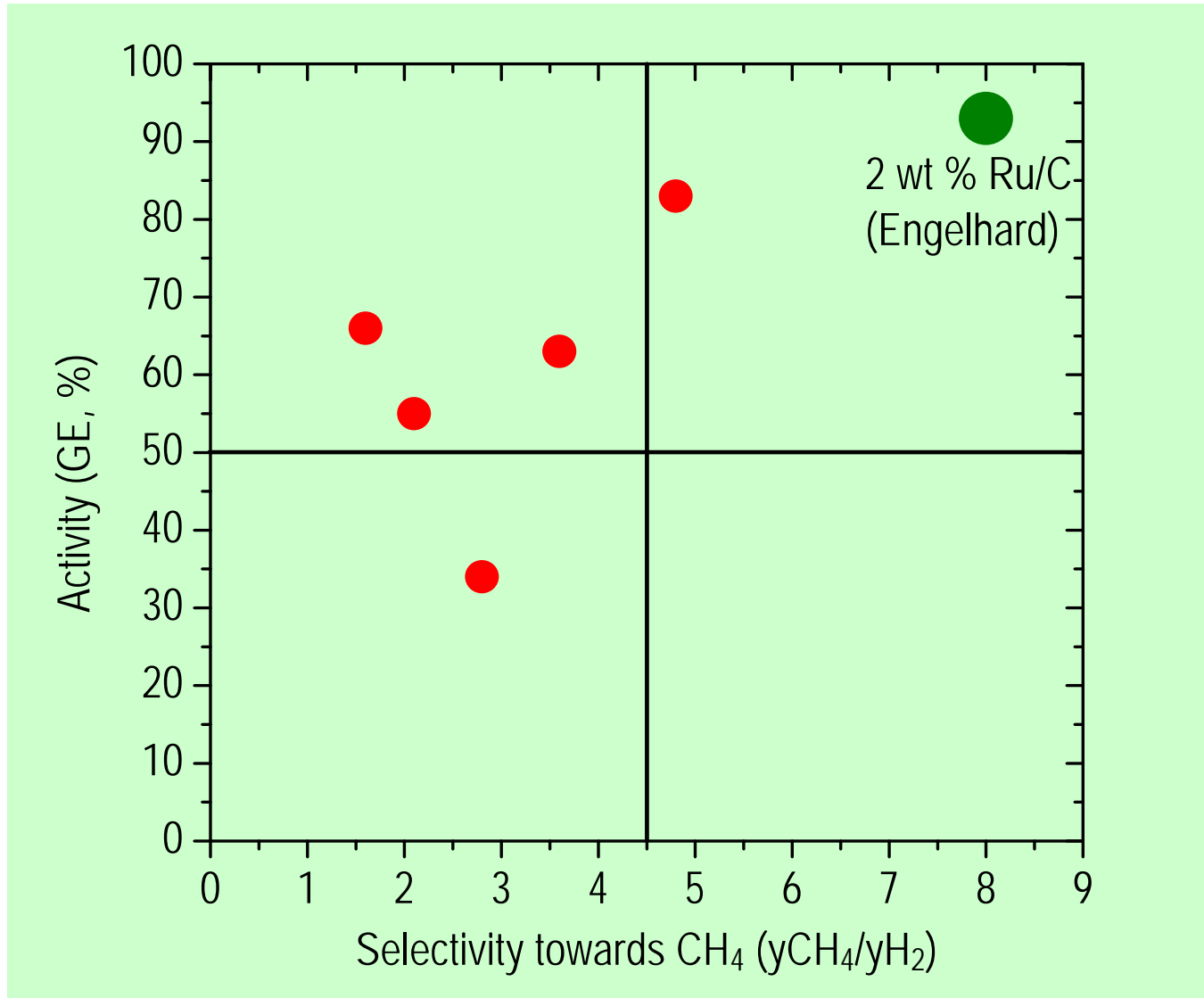
Waldner and Vogel, *I&ECR* 44:13, 2005

Support	Oxidizing	Reducing
$\alpha\text{-Al}_2\text{O}_3$	+	+
HfO_2	+	?
MnO	?	+
MnO_2	(+)	-
Ta_2O_5 (orthorh.)	+	?
TiO_2 (rutile)	+	+
UO_2	+	?
ZrO_2 (monocl. or stab.)	+	+
C (activated carbon)	(+)	+

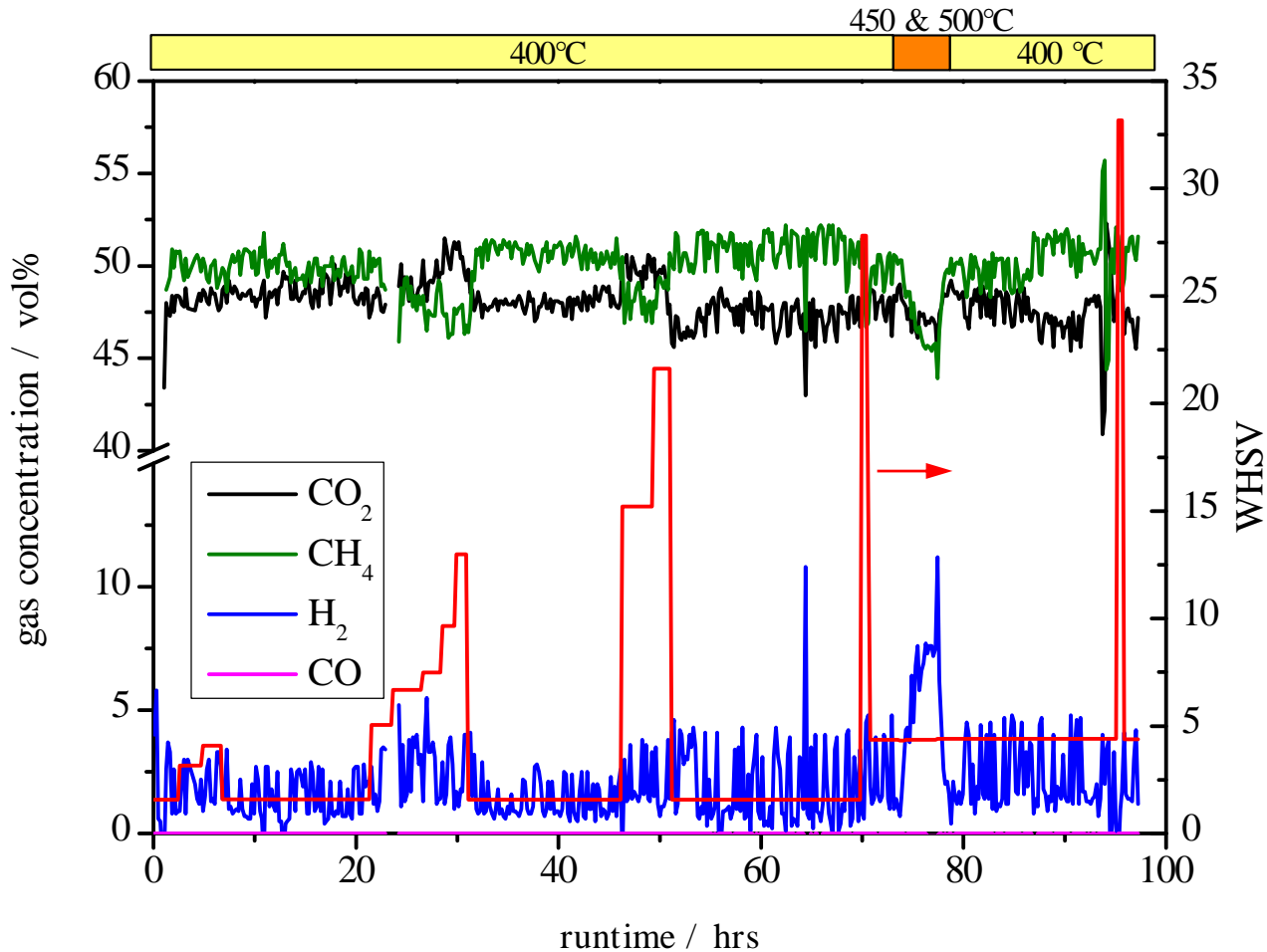
Metal	Oxidizing	Reducing
Ni (stabilized)	-	+
Ru	+	+
Rh	?	+
Pt	(+)	+
Pd	(+)	+

But: strong bases or acids
can cause dissolution!

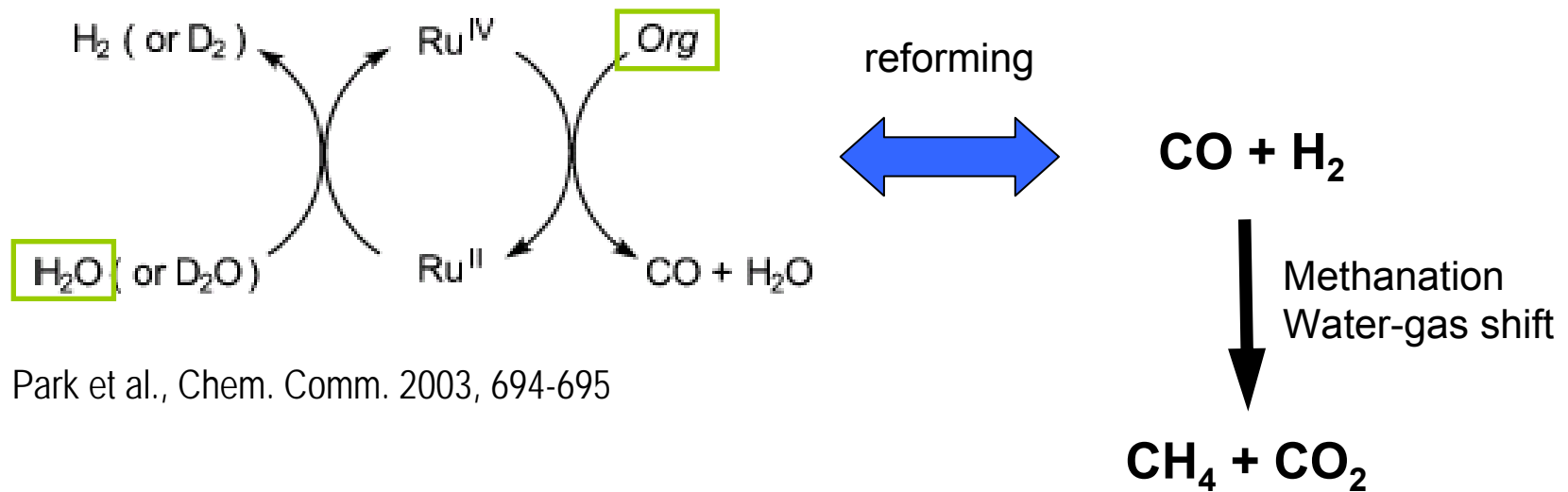
350-500°C, 20-30 MPa, + means active and/or stable, ? not studied



Ru/C catalyst tested for a total of ca. 220 h on stream with a mixture of 5 organic compounds. Accelerated testing with $WHSV_{org}$ up to 33 h^{-1} (red line). Only last 100 h shown.



SCWG of Organic Compounds over Ru: How does the reaction proceed?



Park et al., Chem. Comm. 2003, 694-695

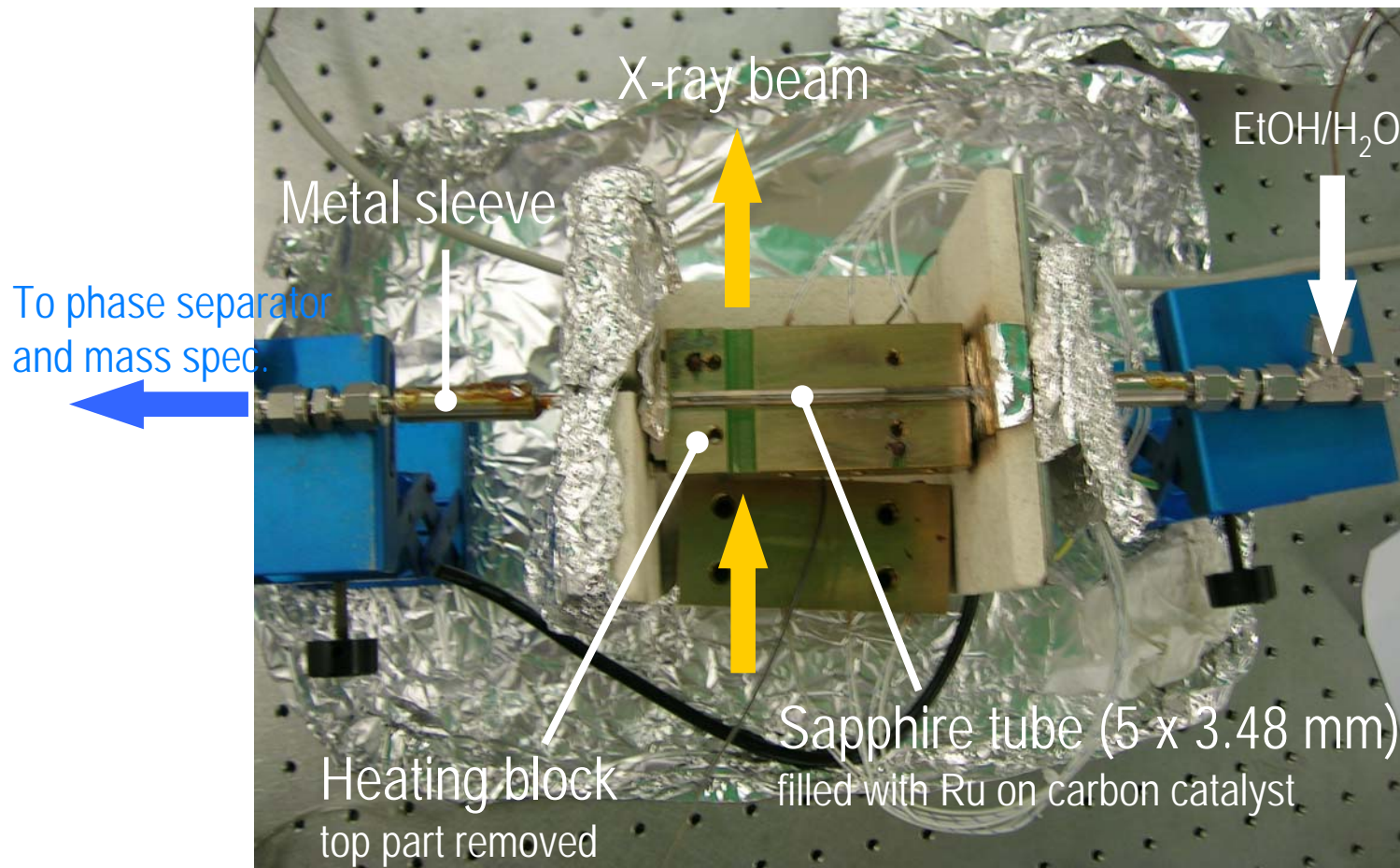
Redox-type reforming reaction $\text{Ru}^{\text{IV}} \Leftrightarrow \text{Ru}^{\text{II}}$?

On which sites does the methanation occur?



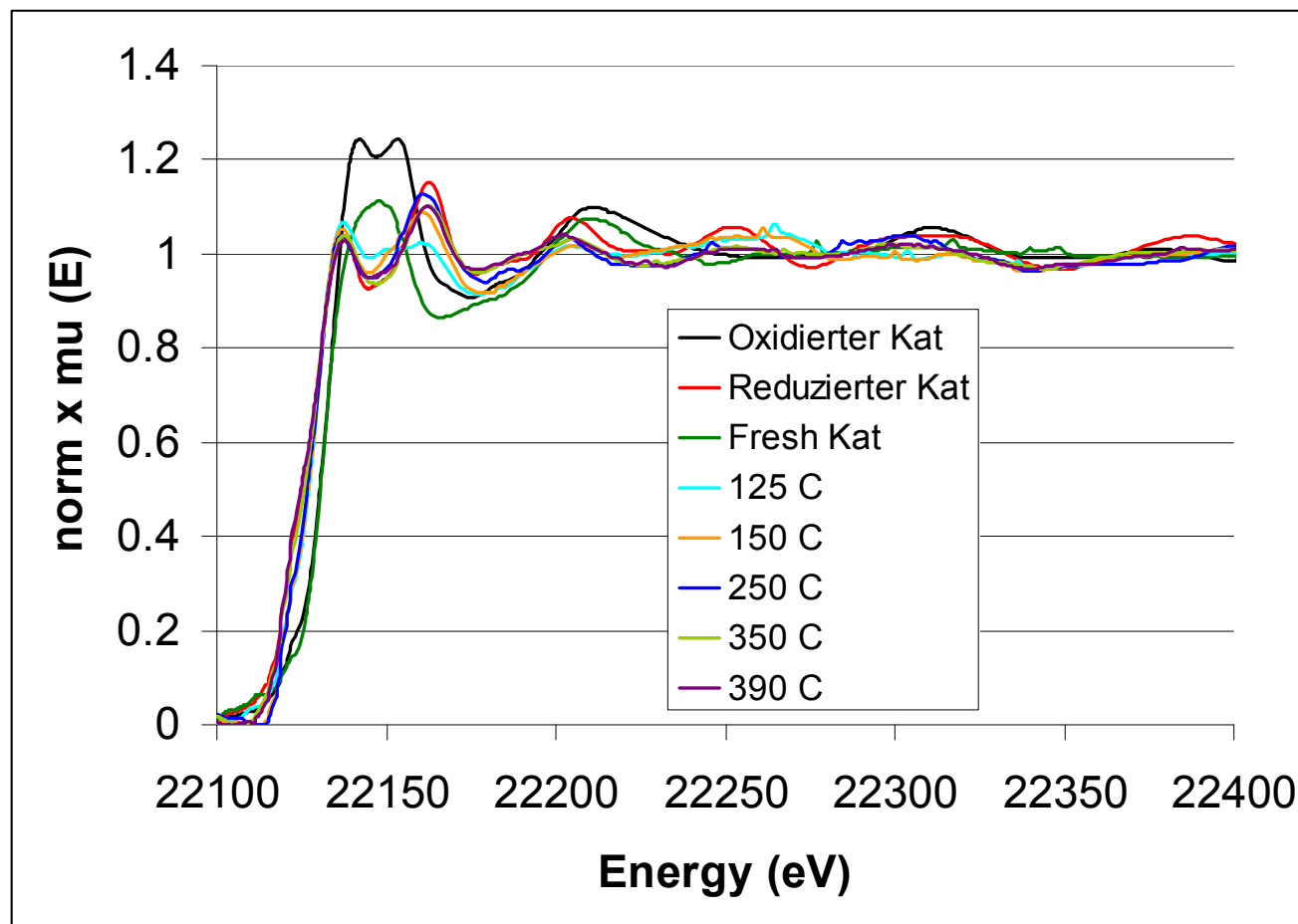
In-situ fixed-bed reactor setup for supercritical water

Sapphire tube glued to metal sleeves

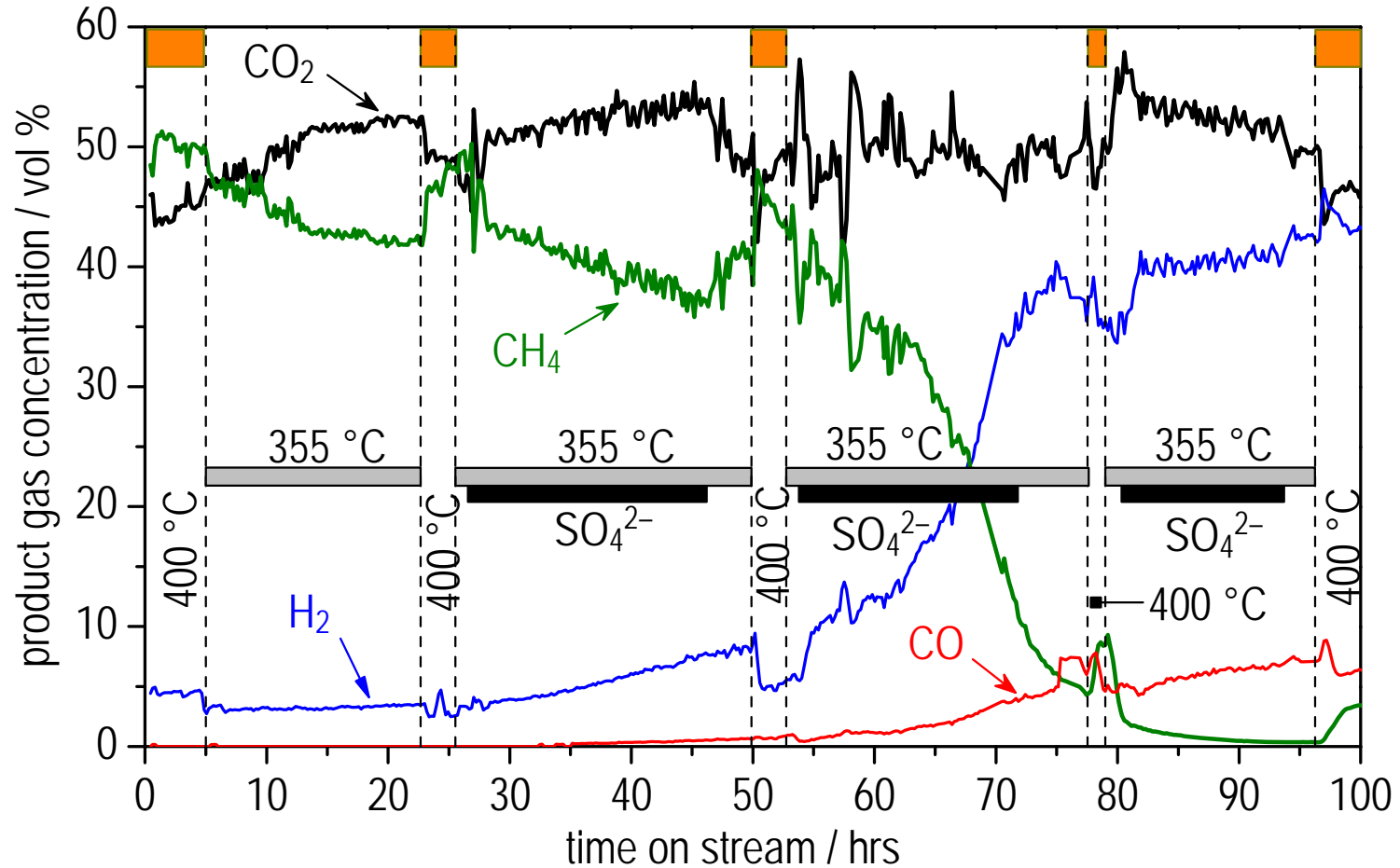


First XAS spectra of a working catalyst in supercritical water

Feed: 5% ethanol/water, catalyst: 2%Ru/C, $p = 250 \pm 6$ bar, SuperXAS beamline at SLS



Organic mixture + 8 ppm sodium sulfate

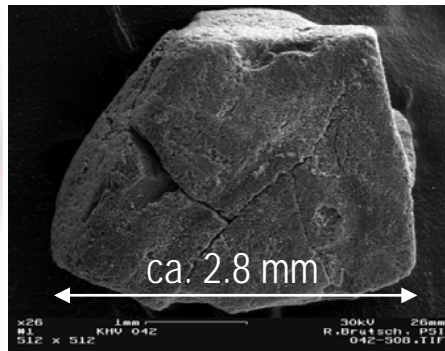


SEM-EDXS examination after sulfate feeding (catalyst deactivated)

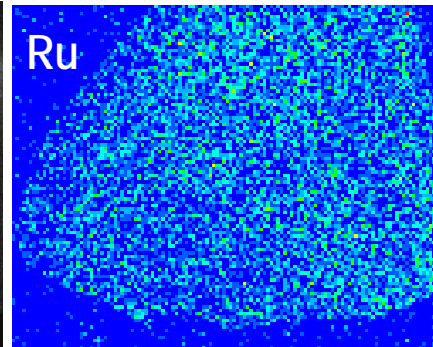
Stereo microscope



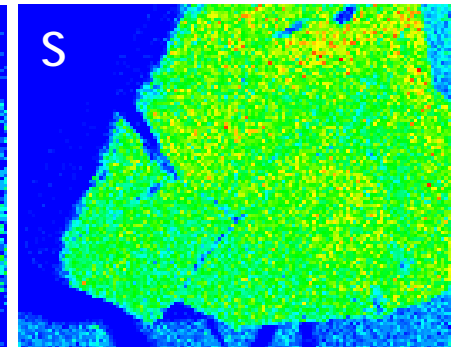
SEM image (SE, 30 keV)



Ru K α EDXS mapping



S K α EDXS mapping



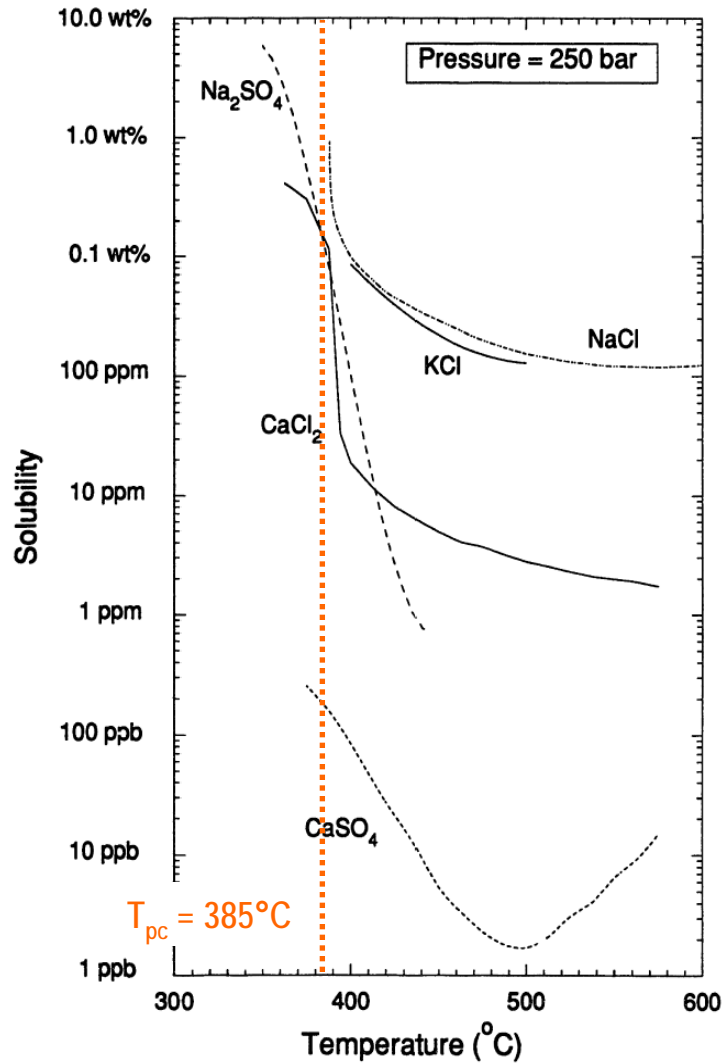
Fe₂O₃ (EDXS)

Al₂O₃ (EDXS)

$$(S / Ru)_{\text{molar}} \approx 1$$

- Sulfur and ruthenium „delocalized“ within the carbon matrix
- XPS identified S species as sulfate. Re-oxidation of sulfide?

SEM analysis by R. Brütsch, PSI



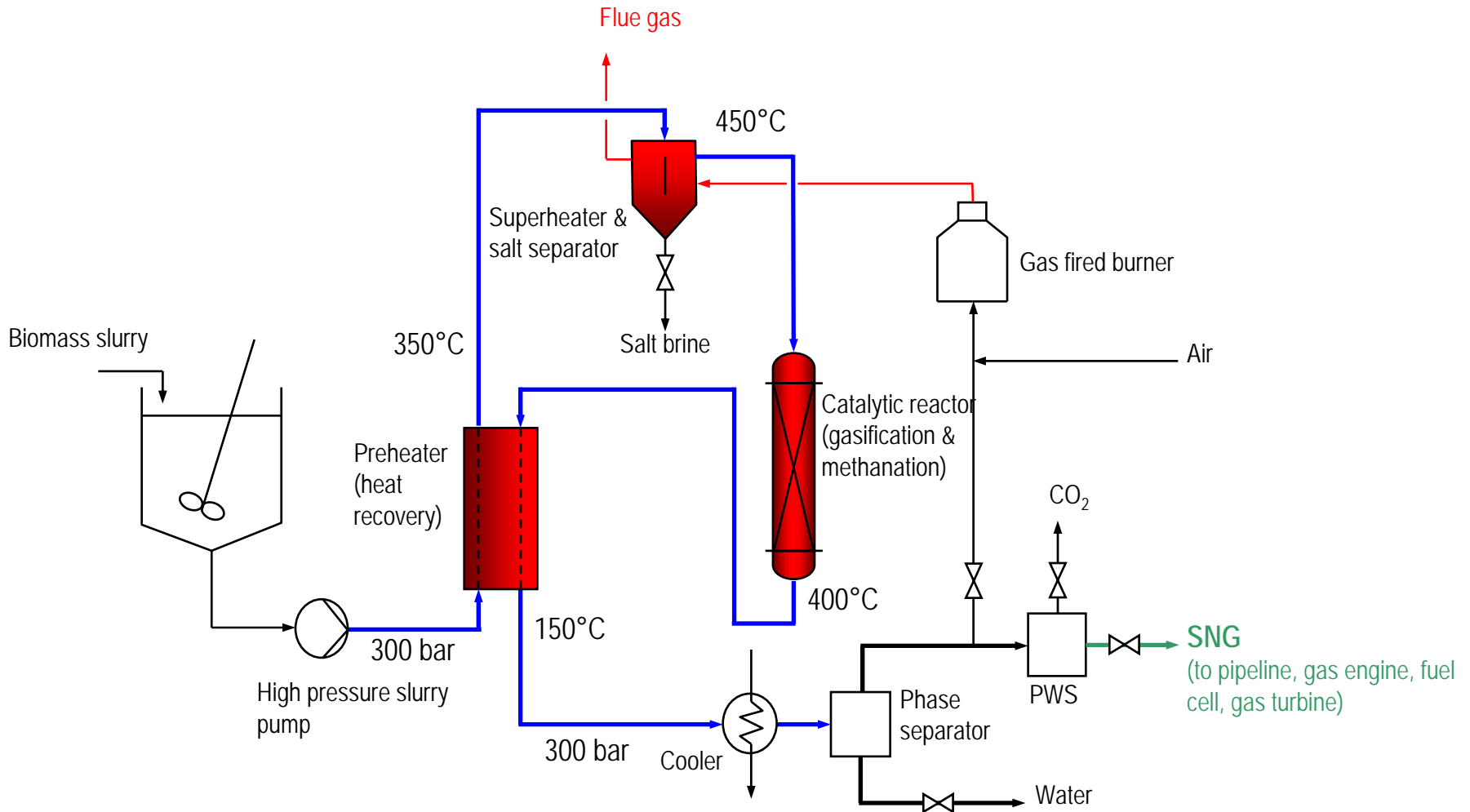
after run

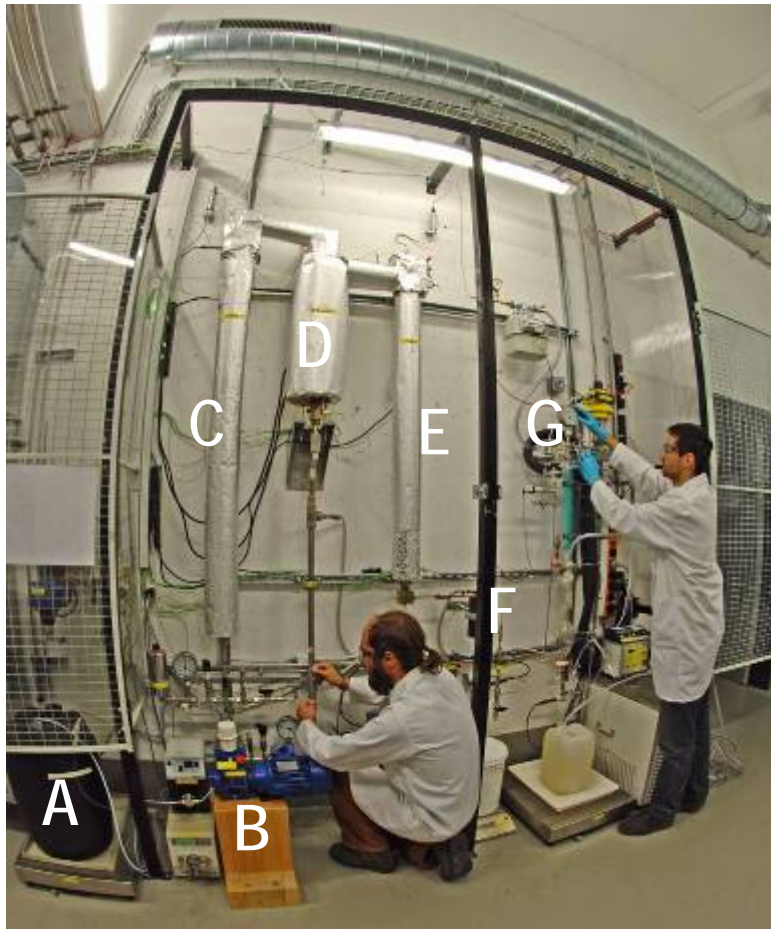


before run

Precipitation of Na₂SO₄ from a 4 wt% solution on a „hot finger“. $T_{\text{solution}} = 356^{\circ}\text{C}$, $p = 25 \text{ MPa}$

Hodes, M. *et al.*, *JSCF* 29 (2004)





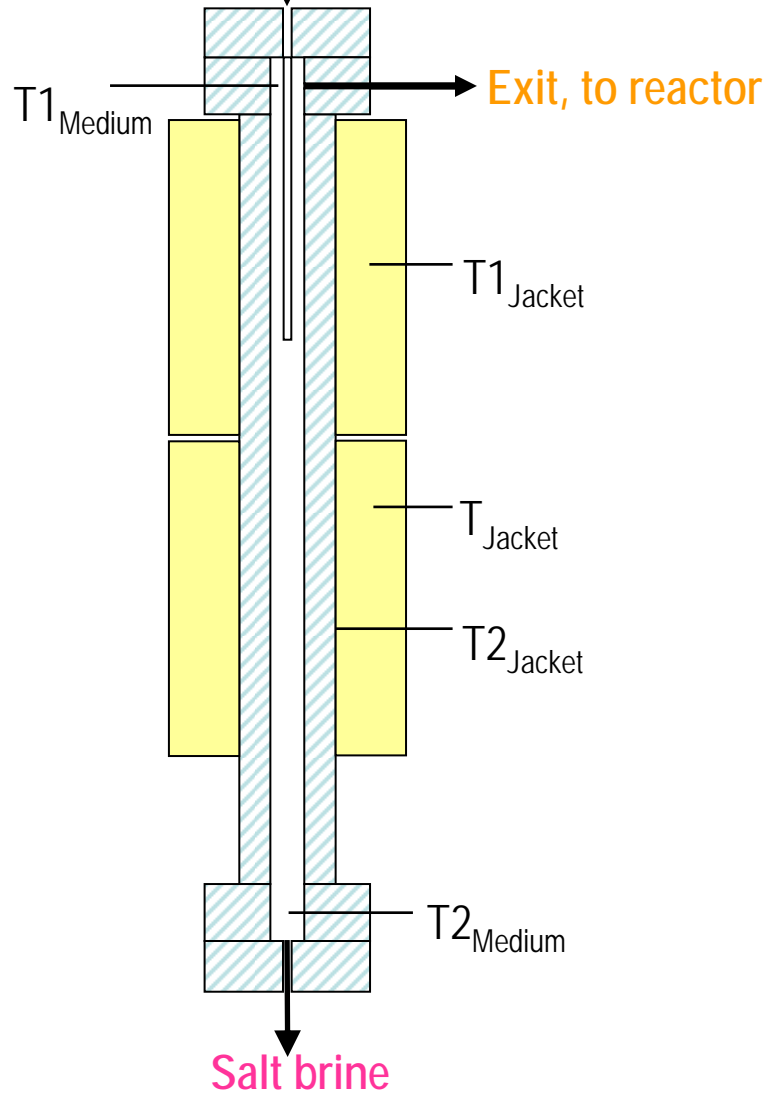
- A Feed container
- B High pressure feed pump
- C Preheater
- D Salt separator
- E Fixed-bed reactor
- F Coolers
- G Pressure letdown & G/L separation
- H on-line gas analysis

Max. 1 kg/h
500°C
350 bar



Salt separator schematic

Feed (salt solution)



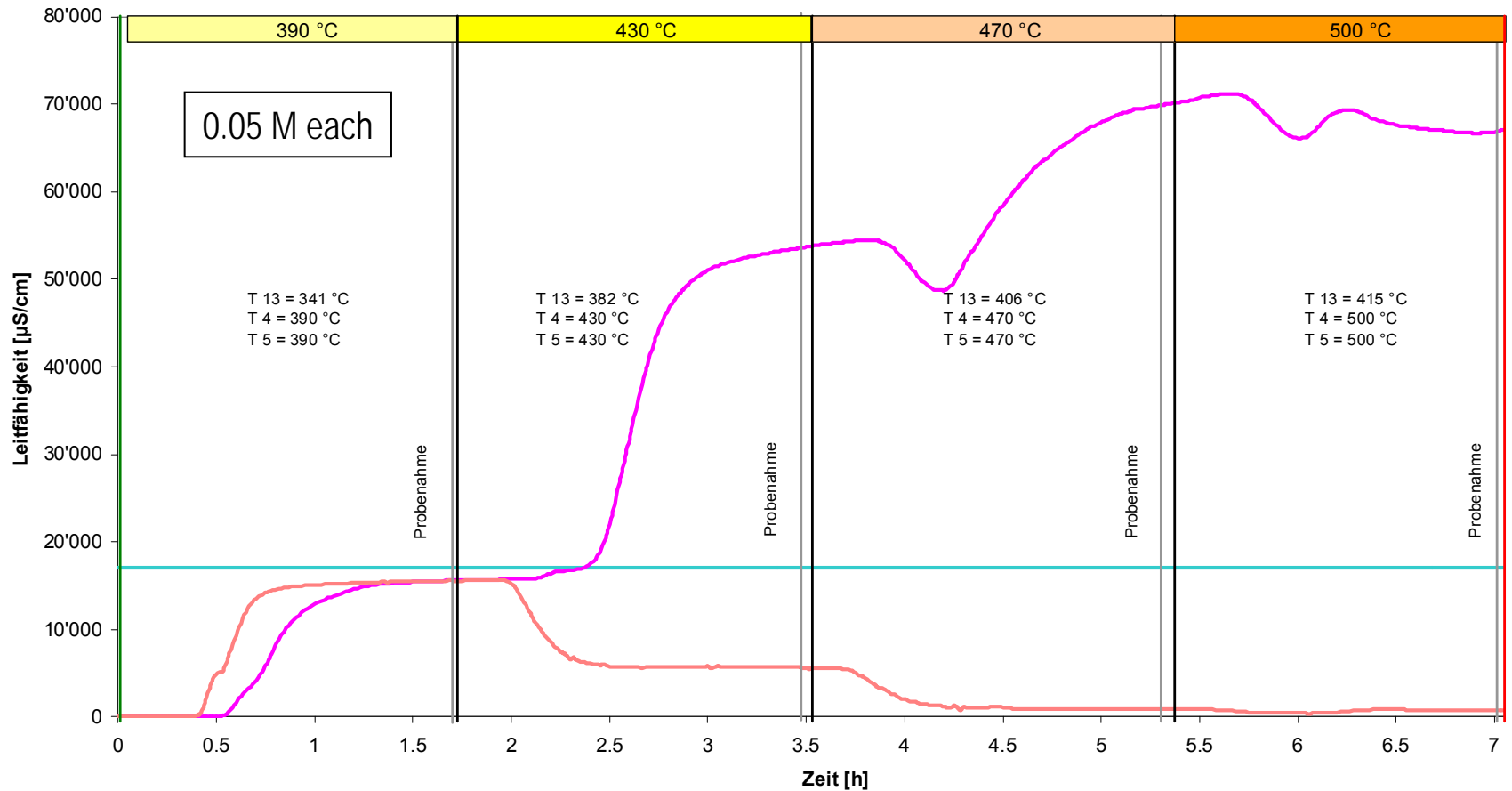
Ti Gr. 5
T _{max} 550°C
ρ _{max} 35 MPa



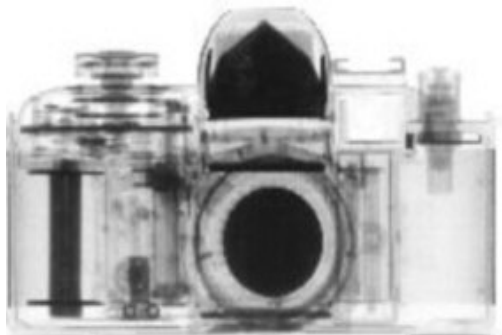
Druck 300 bar
V Feed 960 m/h
m Salzabscheider (SA) ca. 2.6 g/min
Öffnungsverhältnis 1:5 (SA zu V17)

T13 SA Medium oben
T4 SA Mantel oben
T5 SA Mantel unten

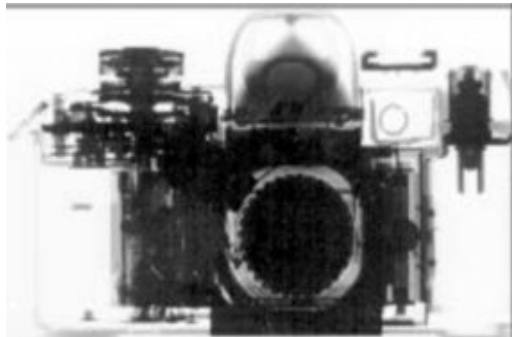
— Feed LF [uS/cm] — LF1 [uS/cm] — LF2 [uS/cm]



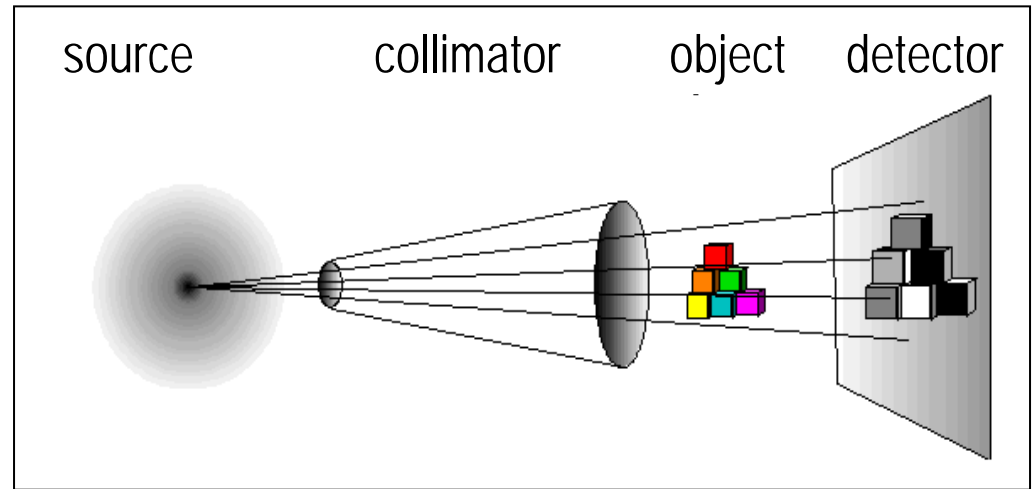
Pictures: ASQ



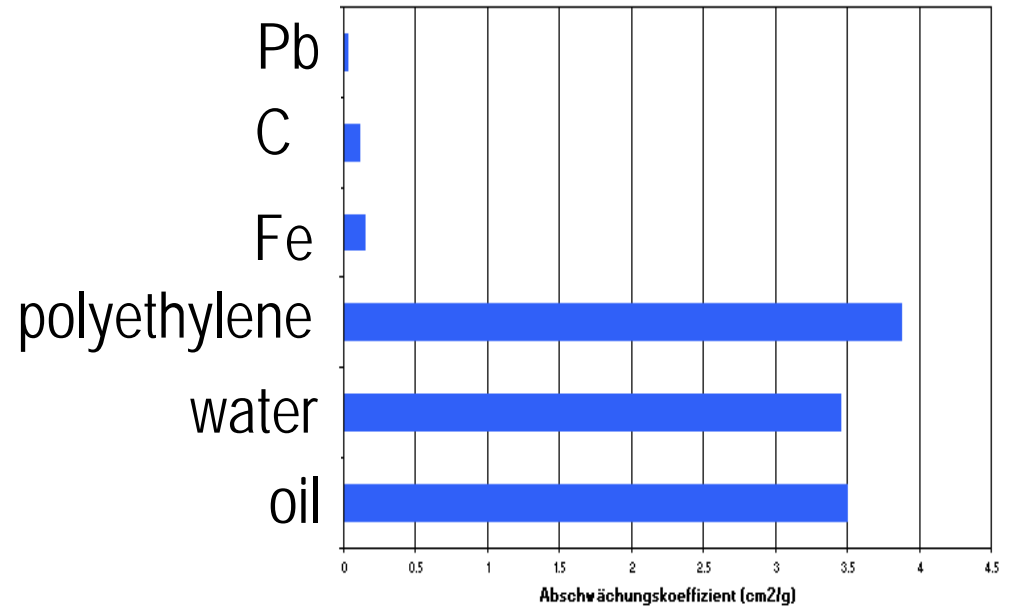
neutrons



X-rays



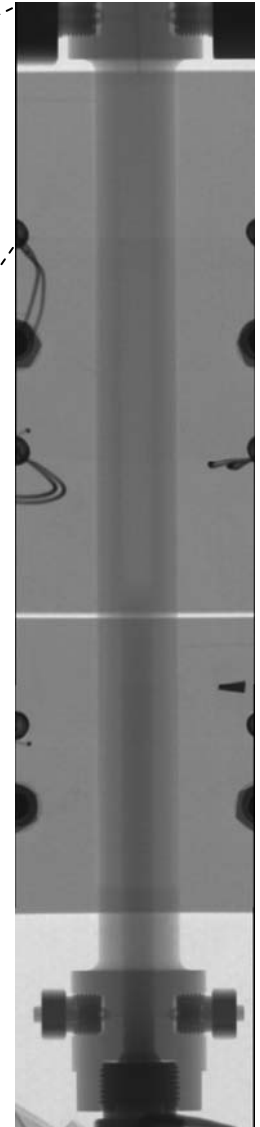
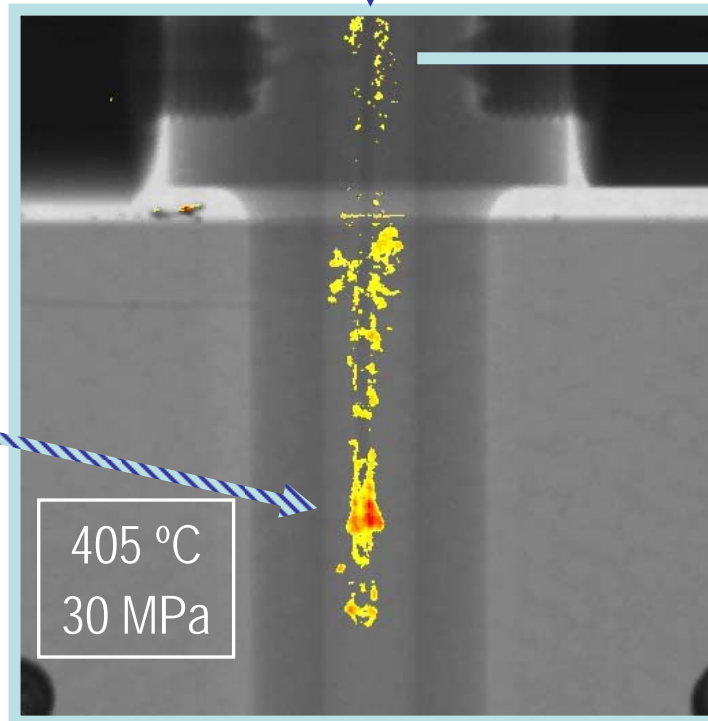
Absorption coefficient



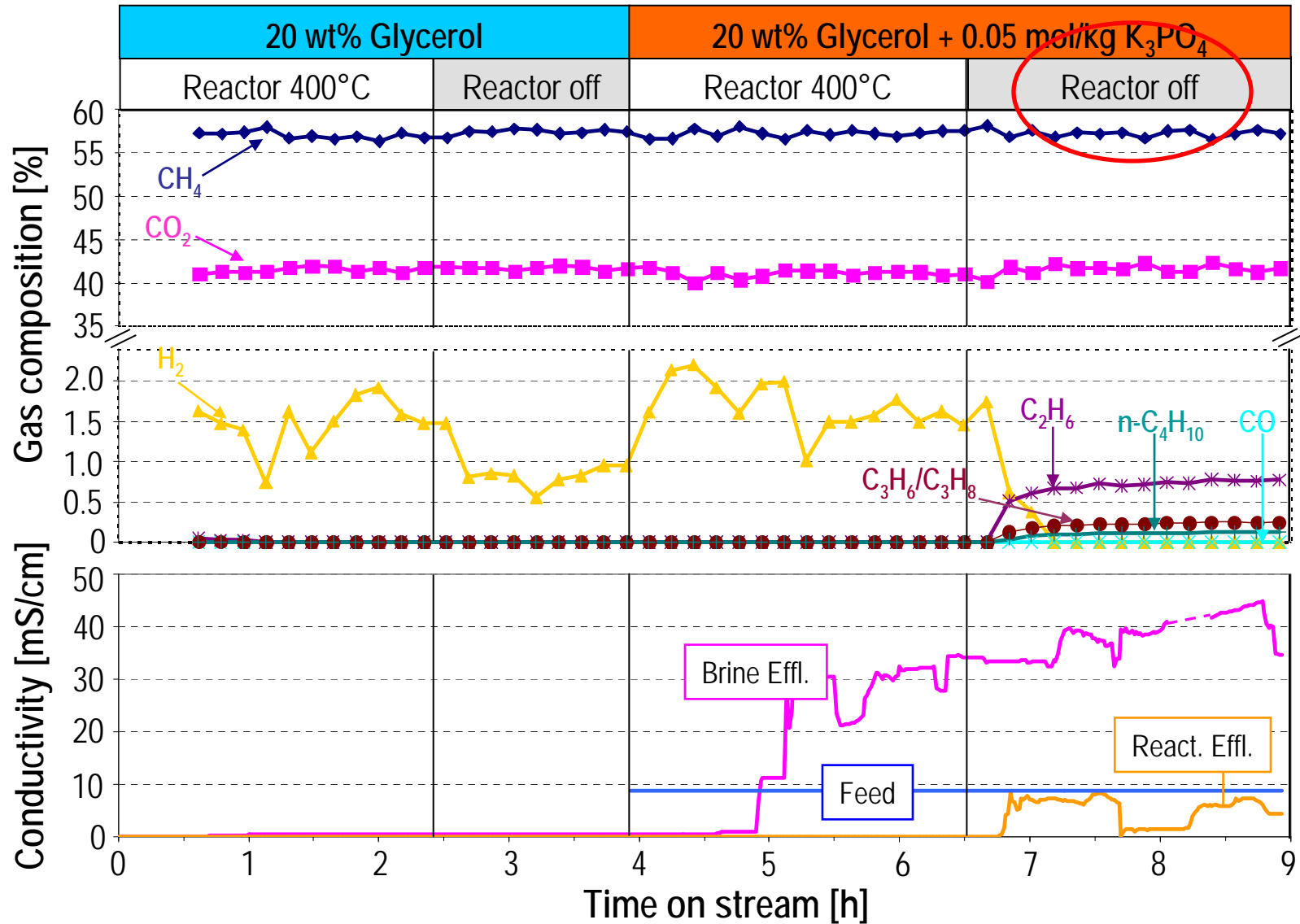
$\text{Na}_2\text{SO}_4/\text{Na}_2\text{B}_4\text{O}_7$ in D_2O



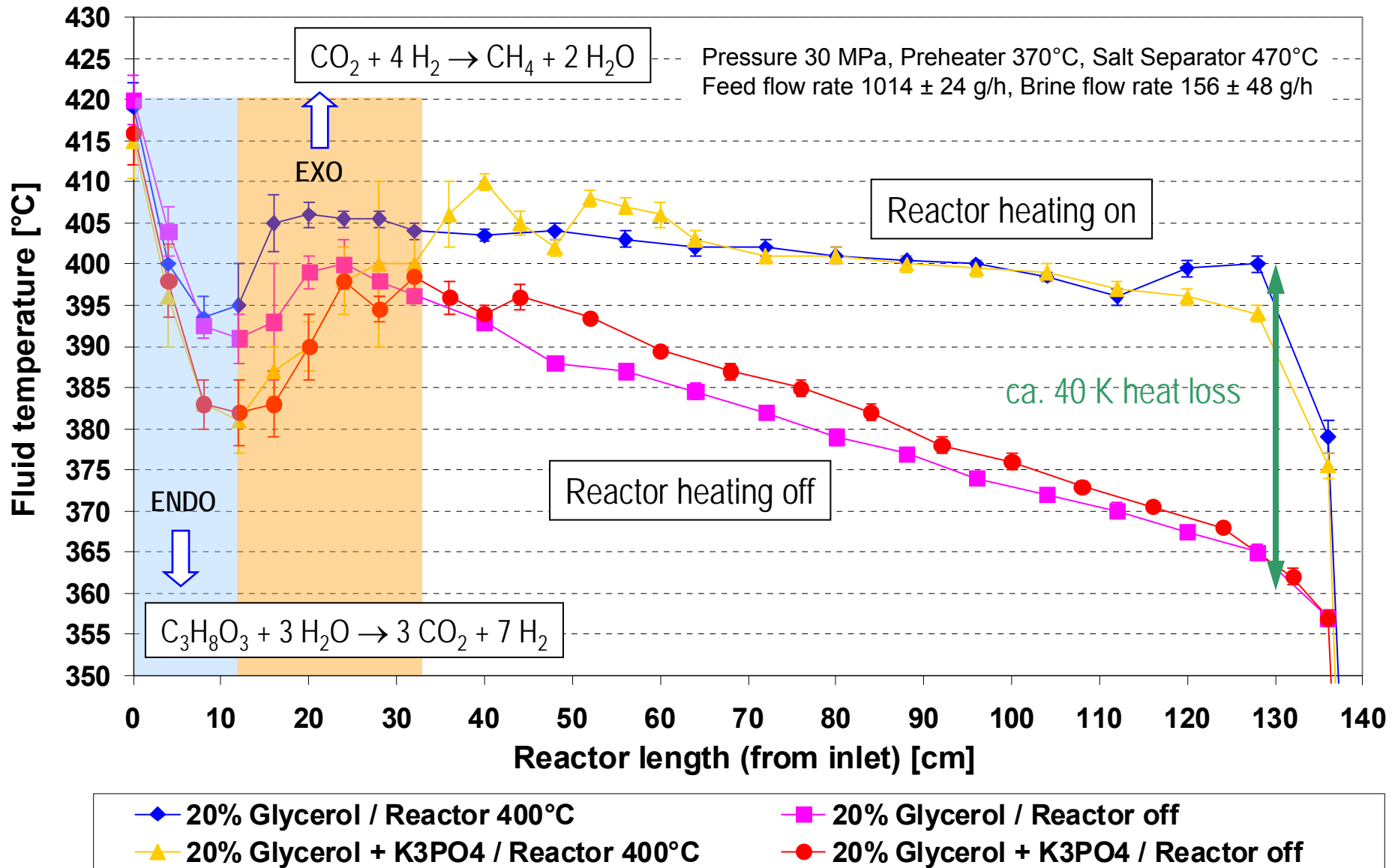
Dip tube outlet



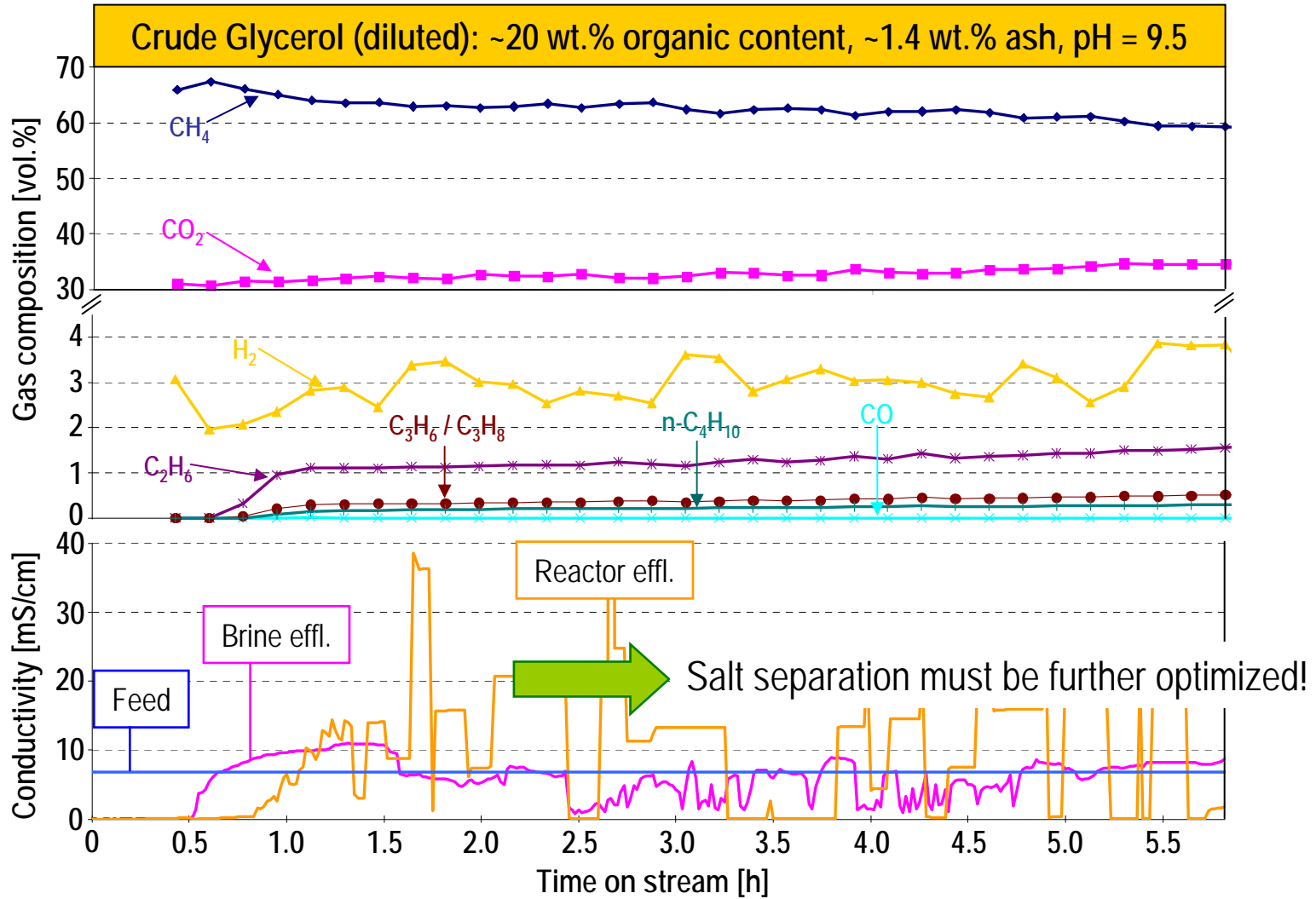
Neutron radiography enables *in-situ* visualization of performance of this supercritical water separator.



Temperature profiles in the catalytic reactor



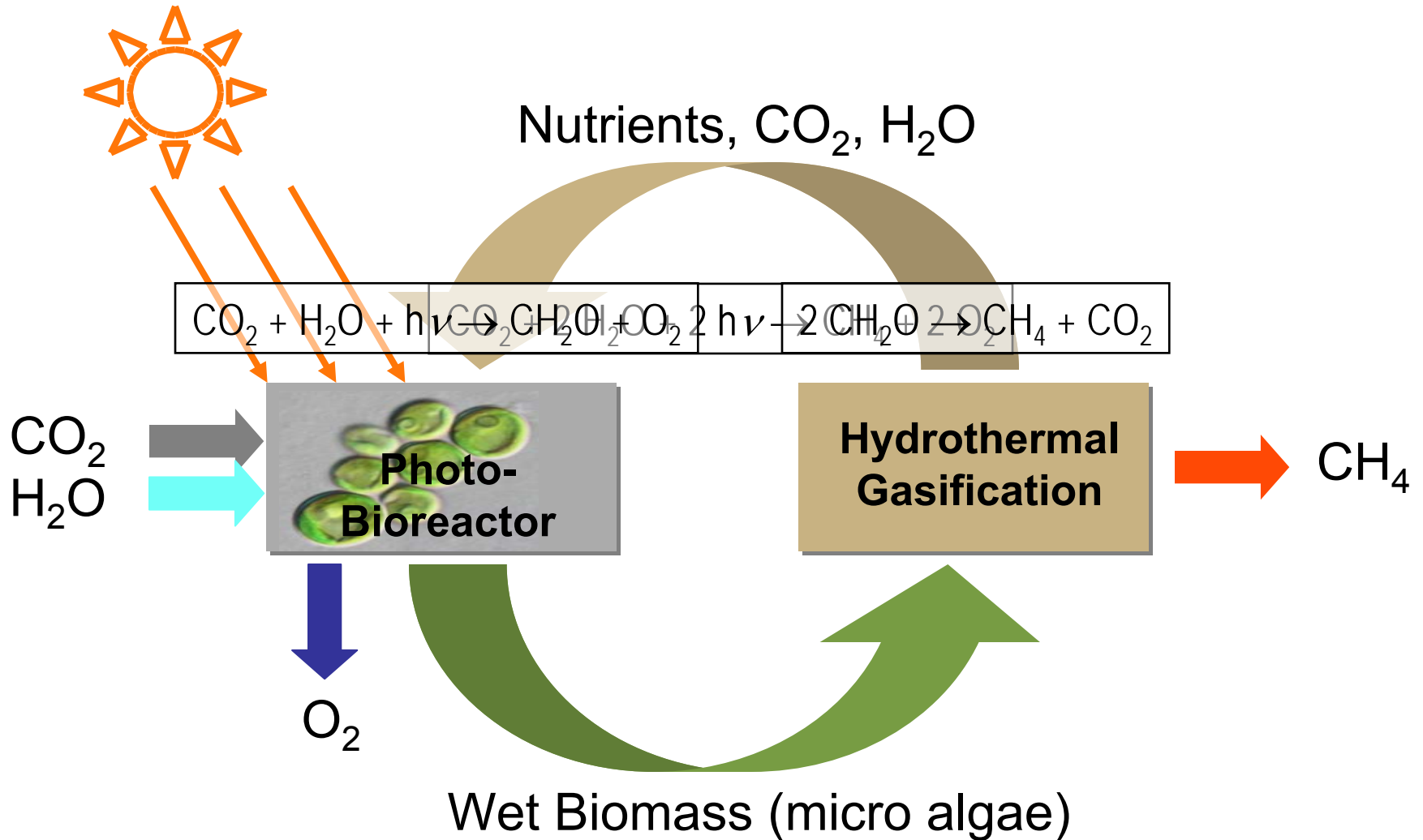
Addressing "real world" challenges



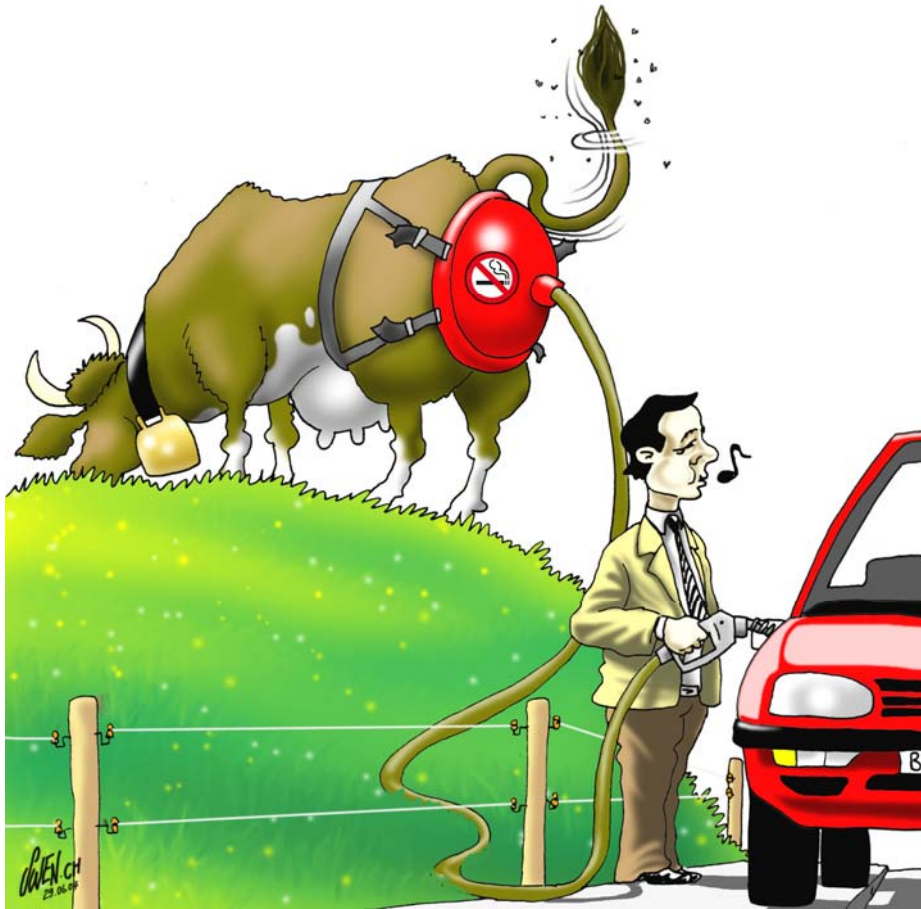
Conditions: - 30 MPa, Preheater 300 °C, Salt Separator 470 °C, Reactor 400 °C
 - Feed flow rate 1015 g/h, Brine effluent flow rate 176 g/h

- The spin-off company **Hydromethan AG** was founded in May 2010 to commercialize PSI's catalytic hydrothermal gasification process.
- Next steps: Pilot plant in Switzerland by 2011 ⇨ Demo plant by 2013
- Size range of commercial plants: ca. 5-50 MW_{biomass}
- Possible feedstocks:
 - Manure
 - Sewage sludge
 - Distillers' dried grains & solubles (DDGS)
 - Fermentation residues (from anaerobic digestion)
 - Algae processing residues
 - Wet organic wastes and sludges from food processing etc.
- Advantages:
 - Full conversion of organic matter to SNG (including woody biomass)
 - Recovery of nutrients as a concentrated brine
 - High net process efficiency biomass-to-SNG of 60-70%
 - SNG can be obtained directly at high pressure (up to 300 bar)
 - Allows processing of a wide range of low-cost wet feedstocks and residues
- Prerequisite: pumpable feed with a minimum of ca. 10 wt% of organic matter

- The resource basis for biomass is **limited**:
 - High area requirement;
 - Agricultural areas are primarily needed for food production;
 - Residual and waste biomass are sustainable resources (with a limited potential)
- Significant extension of sustainable resources only possible if independent of agricultural areas (⇒ **algal biomass**)
- Don't forget: Biomass is the only resource for organic carbon. Production of **materials** and **chemicals** will be a long-term target
 - ⇒ increased competition between biomass for energy and materials and chemicals.



- Water is present in many feedstocks at > 50 wt% and removing it as vapor would require a lot of energy.
- Wet residual biomass is economically attractive but technologically challenging.
- Various types of biomass can be directly gasified to a methane-rich gas in supercritical water using a suitable catalyst (e.g. Ru/C).
- If Bio-SNG is to be produced in an efficient and sustainable way, the separation and recovery of the inorganics (salts) must be considered as well. Ideally, they are a valuable co-product!
- Closed bioenergy systems, based on micro-algae and hydrothermal gasification, are a promising concept for CO₂ mitigation and Bio-SNG production.



It's not that simple...



...but we are working on it!