

# In situ and deactivation studies of the gasification of biomass in super-critical water over Ru/C catalysts

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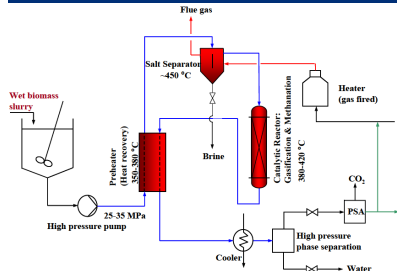
## Introduction

Wet biomass, e.g. agricultural residues, and dry biomass (e.g. wood) are considered playing a major role in our future sustainable energy supply. Biogenic synthetic natural gas (Bio-SNG) is particularly interesting as it can be produced with a high efficiency from almost any kind of biomass applying a proper conversion technology. *Hydrothermal processing* under supercritical water (SCW) conditions does not require dry biomass and thus has a great potential for producing biofuels and bio-chemicals from various types of biomass.

At PSI a SCW process was developed, which is operated at temperatures of 400-450°C and pressures of 25-35 MPa. Presently we feed relatively simple model compounds of wet biomass, e.g. ethanol or glycerol mixtures for investigating supercritical water gasification (SCWG) [1]. The process efficiency was determined to be 66±5 %, and the residency time is < 10 min. The carbon gasification is in the order of > 99% and a yield of ~0.33 g CH<sub>4</sub>/g wood is obtained. As catalyst a commercial 2wt% Ru/C (activated char coal) proved to be efficient and relatively stable against the harsh reaction conditions.

Our research focuses on obtaining an improved insight on the catalyst as well as understanding of the processes and kinetics governing the catalytic reactions in the hydrothermal media and the occasionally observed deactivation.

## Setup's and Analysis



### PSI's SCW process:

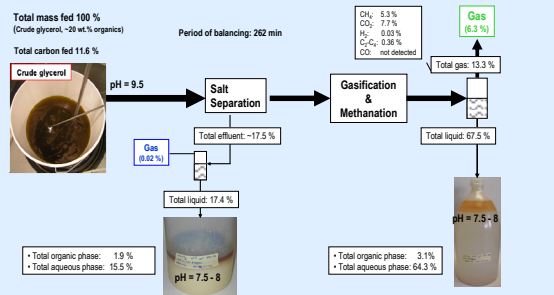
- **pre-heating + liquefaction / 300-370 °C:** break-up of cells, decomposition of large bio-polymers to smaller organic molecules, release of salts and organically bound hetero-atoms (N, P, S) as inorganic compounds
- **super-heating + salt separation / ≤ 450 °C:** continuous precipitation and recovery of released salts
- **catalytic gasification + methanation / ~ 400 °C:** final conversion to mainly CH<sub>4</sub> and CO<sub>2</sub>
- Max. 1 kg/h; T<sub>max</sub> = 773 K, p<sub>max</sub> = 35 MPa

### Applied analytical methods:

- at SLS: **in situ XAS / XES / EXAFS** (super-XAS beamline)
- at ETHZ: **RBS** (2 and 5 MeV He) / **13 MeV <sup>127</sup>I** Heavy Ion **ERDA** / **5 MeV He PIXE** **HAADF-STEM** / **EDX**
- at ENE: **on line QMS/GCMS** **BET** / **Chemisorption** **XPS** (Al Kα mono) **SEM/EDX** **HR-TEM**

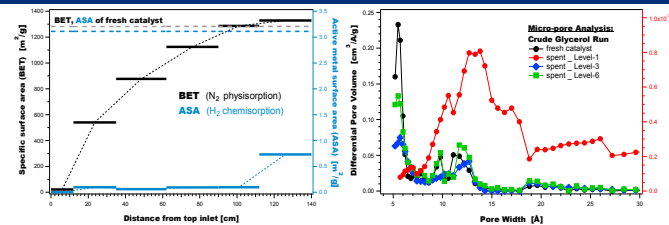
## Results

### Gasification experiments:



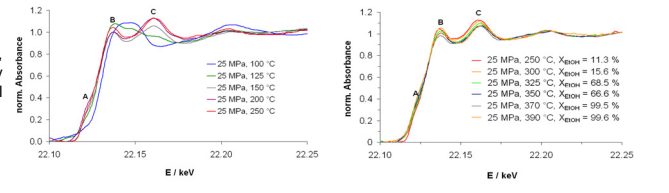
### Surface area determination:

Tremendous loss of ASA and of pore volume



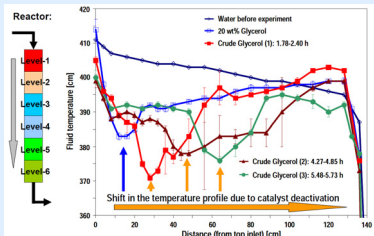
### In situ XANES [3]:

After initial in situ reduction, only Ru<sup>0</sup> as catalytically active species during all states of the SCW reaction



### Crude Glycerol gasification:

Moving deactivation front in direction of the mass flow, shift of the minimum of the fluid temperature inside the reactor.



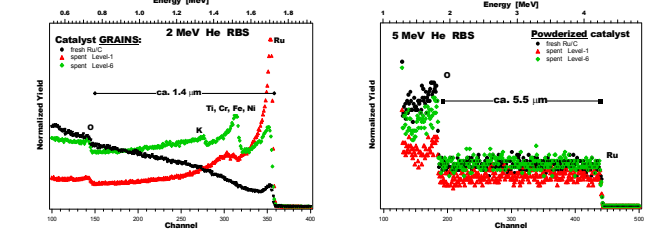
### RBS / EDX / ERDA:

Depth profiling + quantitative element analysis / ~ top 100 nm

- ERDA: EDX: ICP:
- Fresh: 0.7 at% 0.87 at%
- L-1: 0.5 at% 2.3 at% 0.34 at%
- L-6: 2.2 at% 5.4 at% 0.79 at%

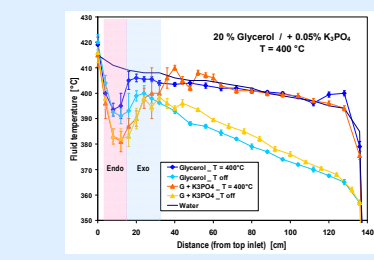
→ Depletion / Dislocation of Ru to end of reactor

→ Surface enrichment: Ru and corrosion products



### Gasification of pure Glycerol / mixtures with salt (K<sub>2</sub>PO<sub>4</sub>):

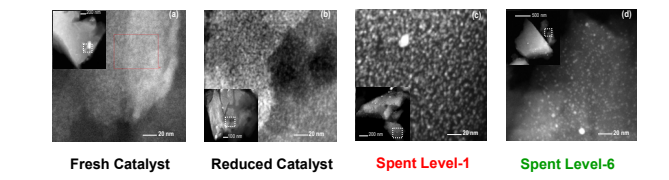
Stable gasification, no shift of the minimum of the fluid temperature inside the reactor.



### HAADF-STEM:

Heavy elements (e.g. Ru) appear as bright contrast

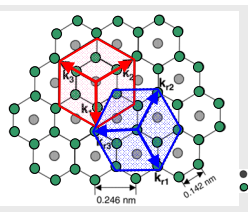
Ru cluster sintering: from 0.7 – 1 nm to 2 – 3 nm



### Literature knowledge [2]:

Ru<sup>2+</sup>: -4.7% / +9.8% mismatch with HOPG lattice two possible Ru lattices rotated relatively by 30°

Lattice constants: RuO<sub>2</sub> = 0.449 nm Graphite = 0.246 nm Ru(0001) = 0.271 nm HOPG = 0.142 / 0.246 nm

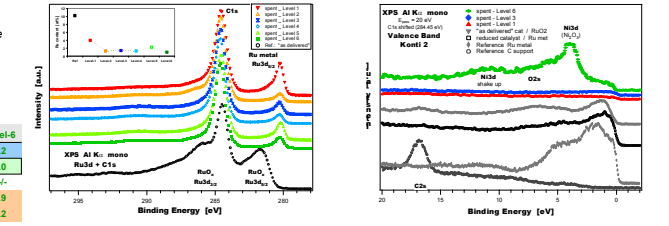


### XPS:

Qualitative and quantitative surface analysis: analysis depth: ~ 2 – 3 nm

- Loss of surface Ru
- Ru<sup>0</sup> + little RuO<sub>2</sub>
- VB: remarkable changes

XPS at%	Ref.	Level-1	Level-3	Level-6
O	26.8	9.3	5.1	4.2
Ru	7.1	3.6	1.4	1.0
P, S, N	0.03/-0.4	0.2/-0.7	-0.6/-	-/-
Ni				0.9
Cr				0.2



## Conclusions

- Catalyst is working; **Ru metal** identified as **active species**
- **Deactivation** sometimes observable, accompanied by:
  - Some **Ru sintering** + **loss of surface area** + **loss of surface Ru**
  - Contamination with minor amounts of **corrosion products** / **other elements**
  - Remarkable **changes** in the **valence band** region

## Acknowledgement

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References:

- [1] M. Schubert, Ph.D. thesis, ETH Zurich, No. 19039 (2010).
- [2] S. Song, T. Cai, J.C. Hanson, J.A. Rodriguez, and J. Hrbek; J. AM. CHEM. SOC. **126** (2004) 8576.
- [3] S. Rabe, M. Nachtgeal, T. Ulrich, F. Vogel; Angew. Chem. Int. Ed. **49** (2010) 1.