Green hydrogen production – An investigation of autothermal reforming of native rapeseed oil

S. Martin, O. Jovalekic, J. Bürkle, A. Wörner

German Aerospace Center (DLR)
Institute of Technical Thermodynamics
Research Group „Alternative Fuels“

Deutsches Zentrum für Luft- und Raumfahrt e.V.
in der Helmholtz-Gemeinschaft

8th European Congress of Chemical Engineering, 25-29 September 2011, Berlin

Table of Contents

Towards a future hydrogen economy

- Requirements of a future hydrogen economy: Sustainability, EU long term commitment (2050): Reduction of emissions by 80-95 %, Low production costs, Simple production process, Availability of feedstock, Avoid food-fuel competition, Consider ecological impacts

A) Biomass

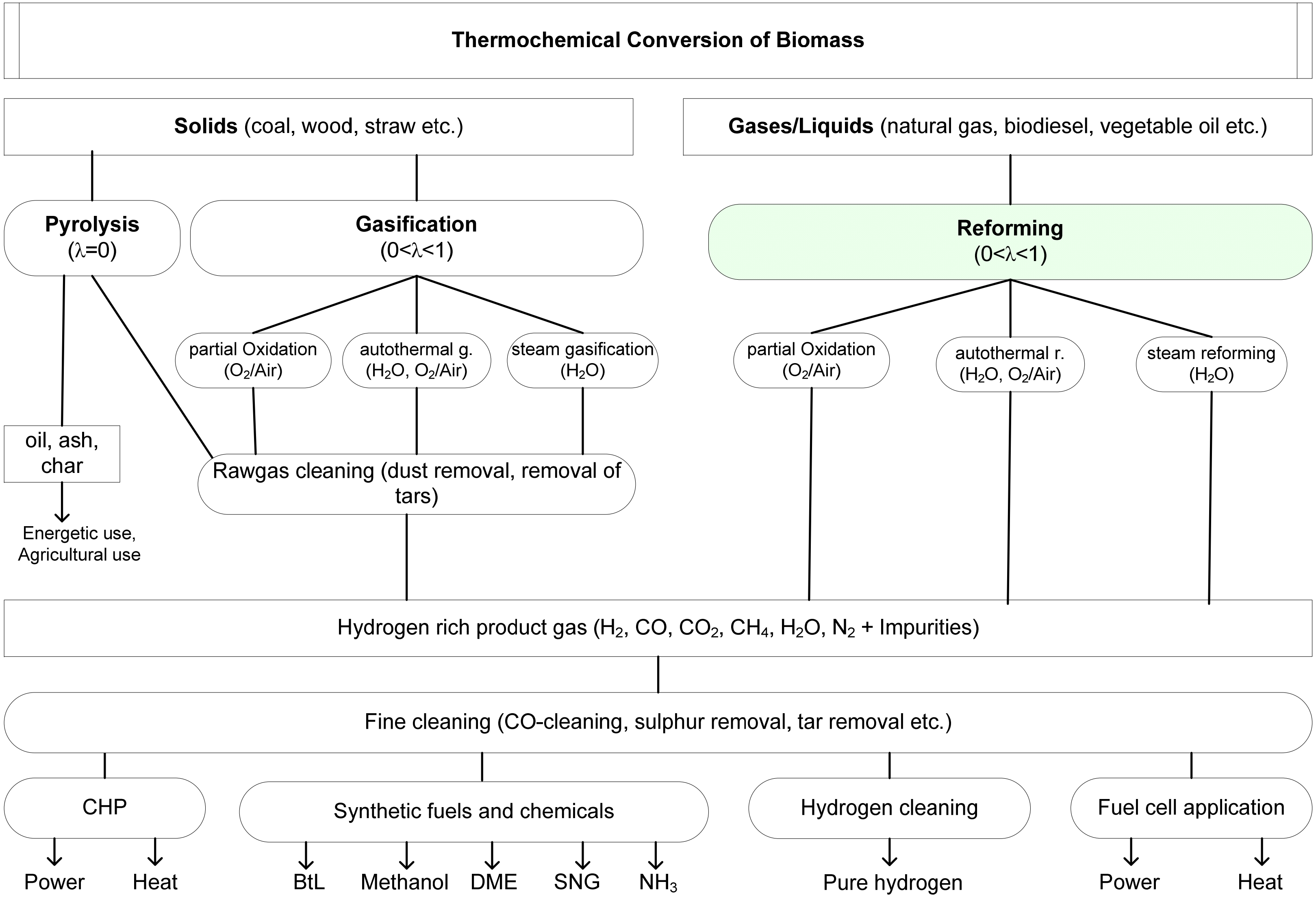
Biological or thermochemical conversion

↓

H_2

B) Renewable Energy

Electrolysis of water → H_2


Thermochemical Conversion of Biomass
Solids (coal, wood, straw etc.)
Gases/Liquids (natural gas, biodiesel, vegetable oil etc.)
Pyrolysis (λ=0)
Gasification (0<λ<1)
Reforming (0<λ<1)
partial Oxidation (O_2/Air)
autothermal g. (H_2O, O_2/Air)
steam gasification (H_2O)
partial Oxidation (O_2/Air)
autothermal r. (H_2O, O_2/Air)
steam reforming (H_2O)
oil, ash, char
Energetic use, Agricultural use
Rawgas cleaning (dust removal, removal of tars)
Hydrogen rich product gas (H_2, CO, CO_2, CH_4, H_2O, N_2 + Impurities)
Fine cleaning (CO-cleaning, sulphur removal, tar removal etc.)
CHP
Synthetic fuels and chemicals
Hydrogen cleaning
Fuel cell application
Power
Heat
BtL
Methanol
DME
SNG
NH_3
Pure hydrogen
Power
Heat

Biofuels in Germany (2010)

available biofuels on the market:

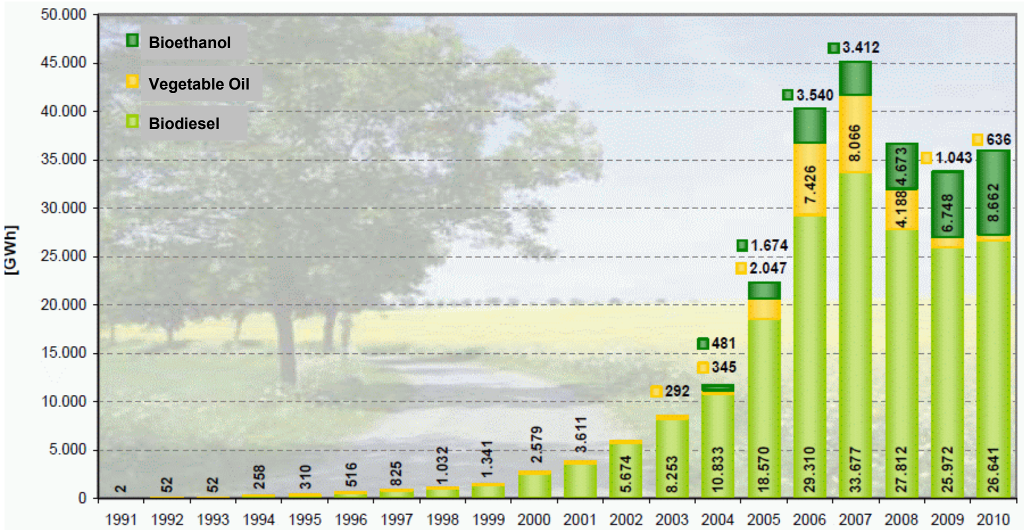
- **Vegetable oil**
- **Biodiesel**
- **Bioethanol**

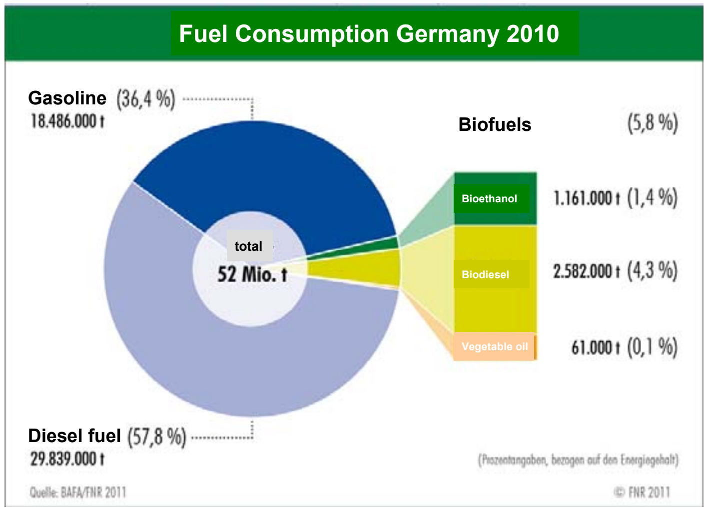
} 1. Generation Biofuels

not available on the market:

- Synthetic Biofuels (BtL, MtS etc.)
- Cellulosic Ethanol
- Bio SNG

} 2. Generation Biofuels

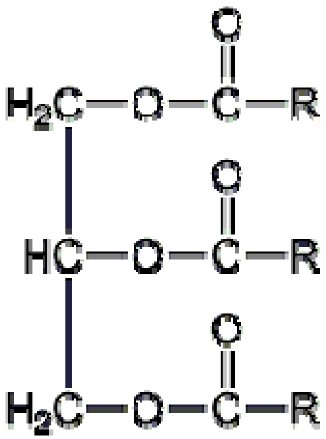




⇨ Vegetable Oil as a promising option for green hydrogen production

Vegetable Oil

- Dominating vegetable oil in Europe and Germany: **Rapeseed oil**
- Area under cultivation in Germany (2010): 1,5 Mio ha
- Oil yield / hectare: ~1500 l/(ha·a) → 2 Mio tons rapeseed oil
- High volumetric and gravimetric density (comparable to fossil fuels)
- Simple production process
- Low sulphur content



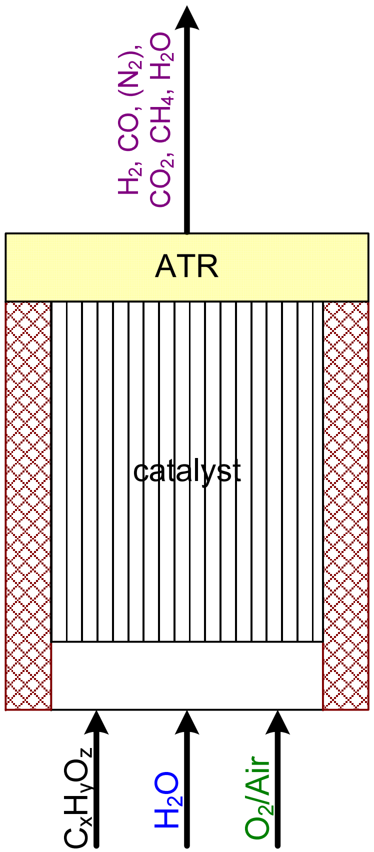
Chemical Structure

Fatty Acid (R)	**Total formula (Number of carbon atoms: double bonds)**	**Percentage**
Oleic Acid	$C_{18}H_{34}O_2$ (18:1)	51-70%
Linolic Acid	$C_{18}H_{32}O_2$ (18:2)	15-30%
Linolenic Acid	$C_{18}H_{30}O_2$ (18:3)	5-14%

→ Chemical formula: $C_{56,9}H_{101,8}O_6$

→ Model Substance Trioleate: $C_{57}H_{104}O_6$ (R=Oleic Acid)

ATR of Rapeseed Oil – Chemical Reaction System



Steam reforming reaction

$C_{57}H_{104}O_6 + 51\ H_2O \rightarrow 57\ CO + 103\ H_2$ $\Delta H_{700°C} = 8337$ kJ/mol

Partial oxidation reaction

$C_{57}H_{104}O_6 + 25{,}5\ H_2O \rightarrow 57\ CO + 52\ H_2$ $\Delta H_{700°C} = -4296$ kJ/mol

Total oxidation reaction

$C_{57}H_{104}O_6 + 80\ H_2O \rightarrow 57\ CO_2 + 52\ H_2O$ $\Delta H_{700°C} = -33294$ kJ/mol

Methanation reaction

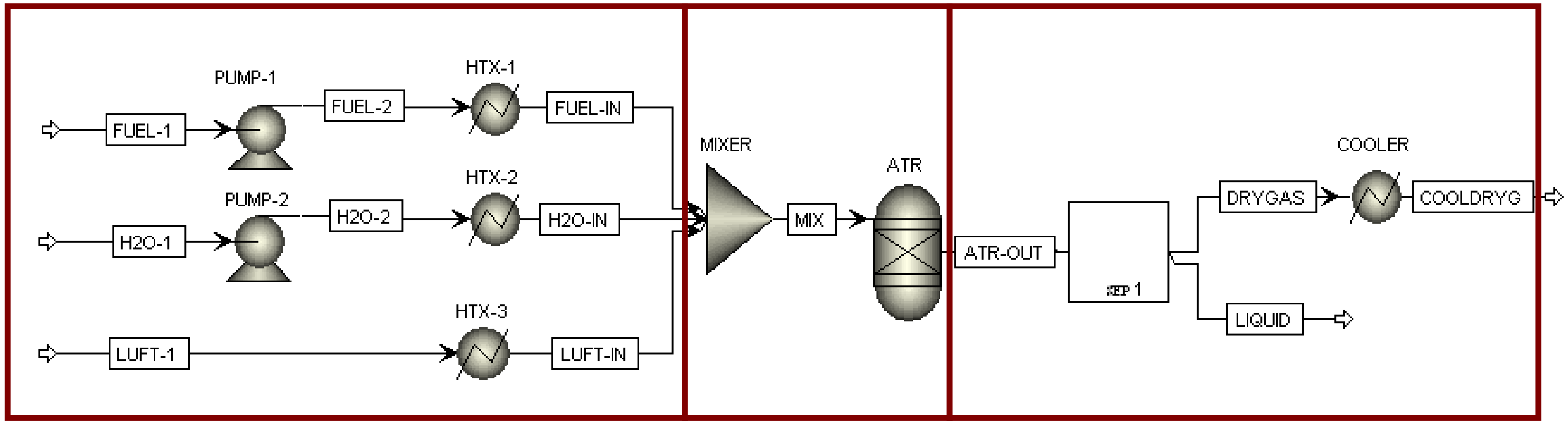
$CO + 3\ H_2 \rightarrow CH_4 + H_2O$ $\Delta H_{700°C} = -165$ kJ/mol

Water gas shift reaction

$CO + H_2O \rightarrow H_2 + CO_2$ $\Delta H_{700°C} = -125$ kJ/mol

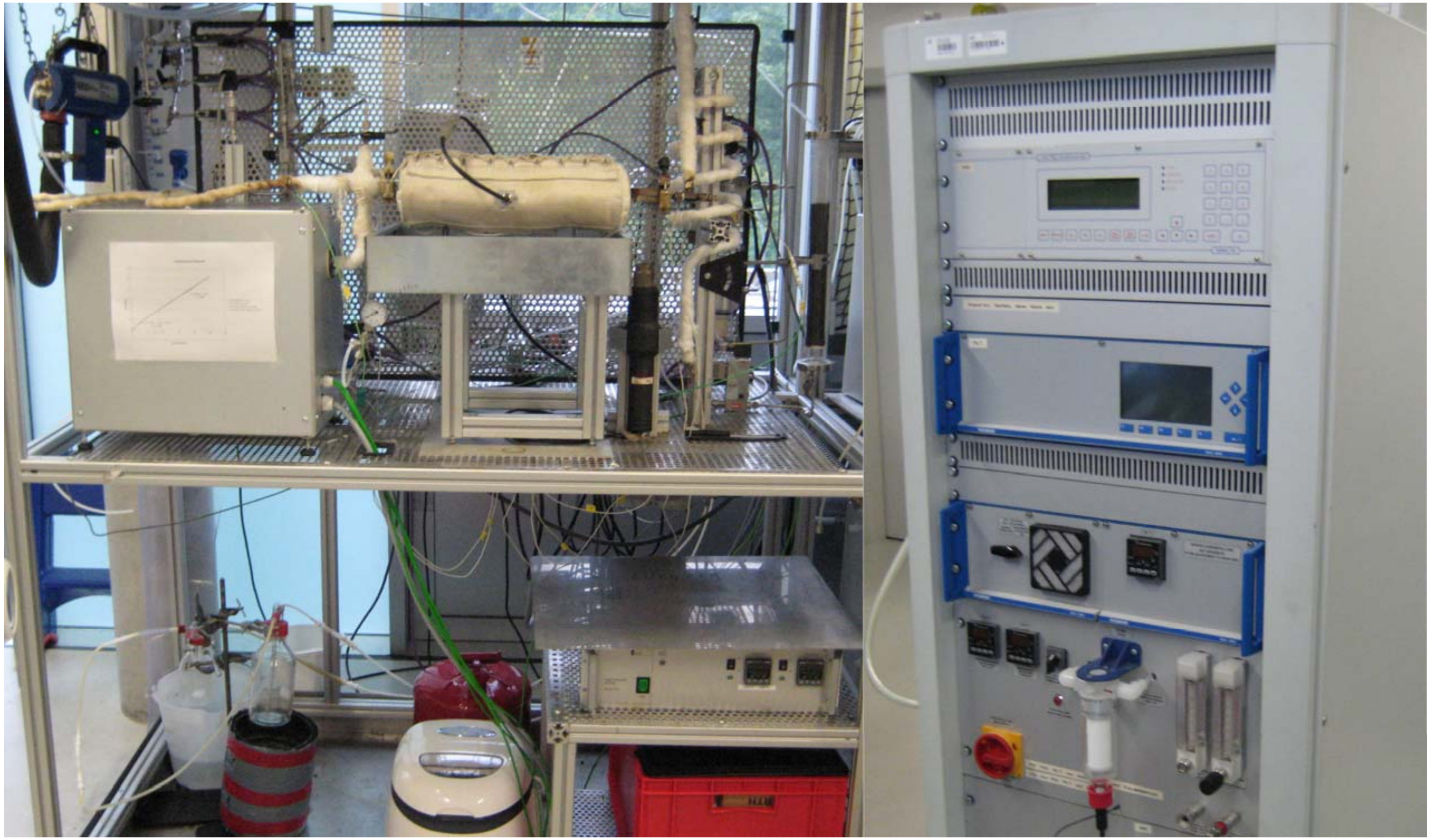
Simulation of ATR with Aspen Plus®

- Aspen Plus Flowsheet of autothermal rapeseed oil reforming

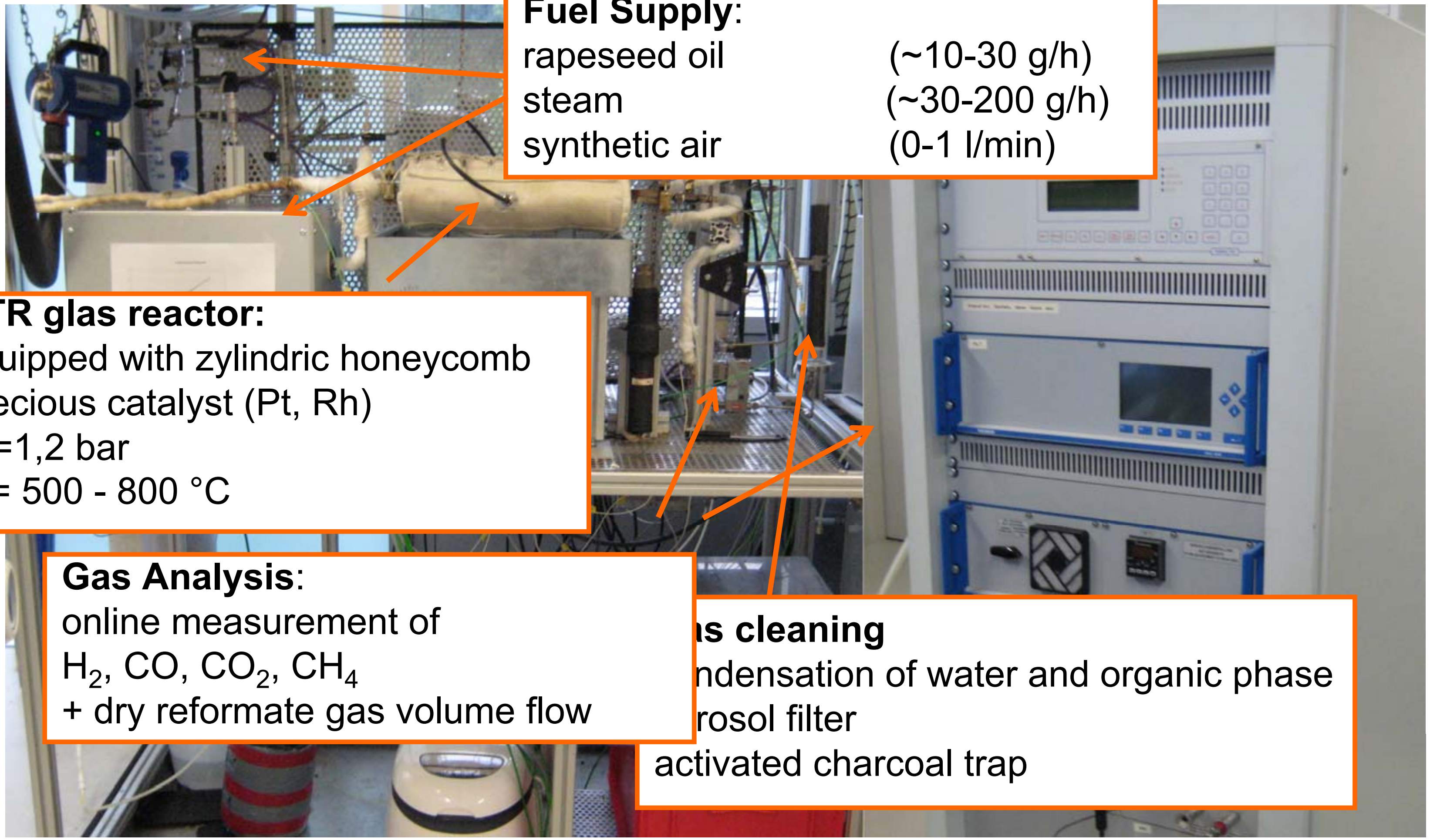


Fuel Supply	**ATR Reactor**	**Condensation of Liquids**
rapessed oil steam synthetic air	chemical Equilibrium using „Gibbs“-Reactor	water and organic phase

Experimental Test Setup



Experimental Test Setup



Fuel Supply:
rapeseed oil (~10-30 g/h)
steam (~30-200 g/h)
synthetic air (0-1 l/min)

ATR glas reactor:
equipped with zylindric honeycomb
precious catalyst (Pt, Rh)
P =1,2 bar
T = 500 - 800 °C

Gas Analysis:
online measurement of
H_2, CO, CO_2, CH_4
+ dry reformate gas volume flow

…s cleaning
…ndensation of water and organic phase
…rosol filter
activated charcoal trap

Process variables and evaluation

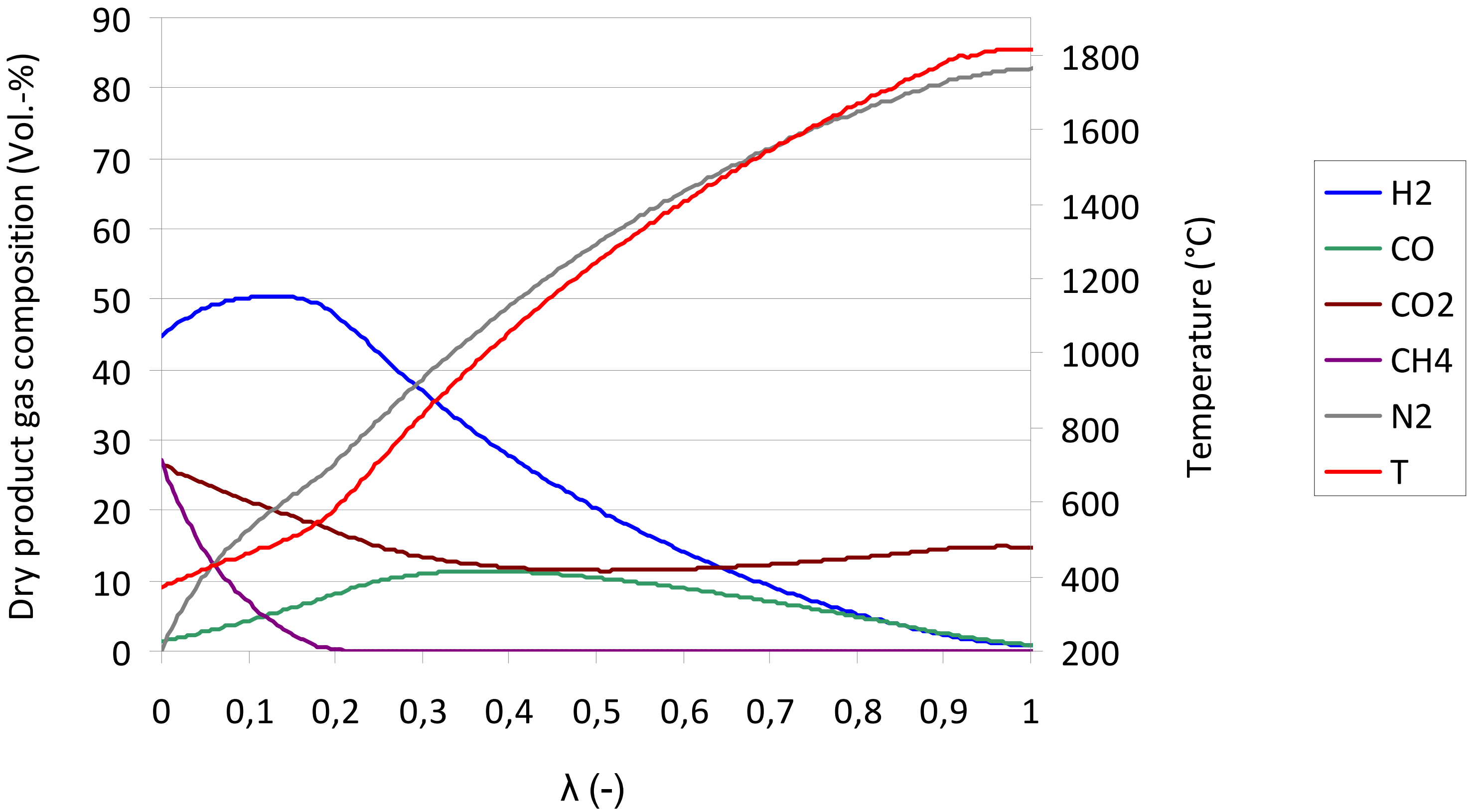
- Steam to carbon ratio $\frac{S}{C} = \frac{\dot{n}_{H_2O}}{\dot{n}_{C,rapeseedoil}}$
- Air ratio $\lambda = \frac{\dot{n}_{O_2}}{\dot{n}_{O_2,stochiometric}}$
- Gas Hourly Space Velocity $GHSV = \frac{\dot{V}_{feed}}{V_{reactor}}$

} independant process variables

- Energetic H_2-efficiency $\eta_t = \frac{\dot{m}_{H_2}(t) \cdot H_{u,H_2}}{\dot{m}_{rapeseedoil} \cdot H_{u,rapeseedoil}}$ $\eta_0 = \frac{\dot{m}_{H_2}(t=0) \cdot H_{u,H_2}}{\dot{m}_{rapeseedoil} \cdot H_{u,rapeseedoil}}$
- Mass balance $\dot{m}_{C_{57}H_{104}O_6} + \dot{m}_{H_2O} + \dot{m}_{Air} = \dot{m}_{reformate} + \dot{m}_{condensate,organic} + \dot{m}_{condensate,H_2O}$
- Feed Conversion $FC = 1 - \frac{\dot{m}_{cond.,organic}}{\dot{m}_{rapeseedoil}}$ $CC = 1 - \frac{m_{C,reformate}}{\dot{m}_{C,rapeseedoil}}$
- Deactivation $D = 1 - \frac{\eta_t}{\eta_0}$

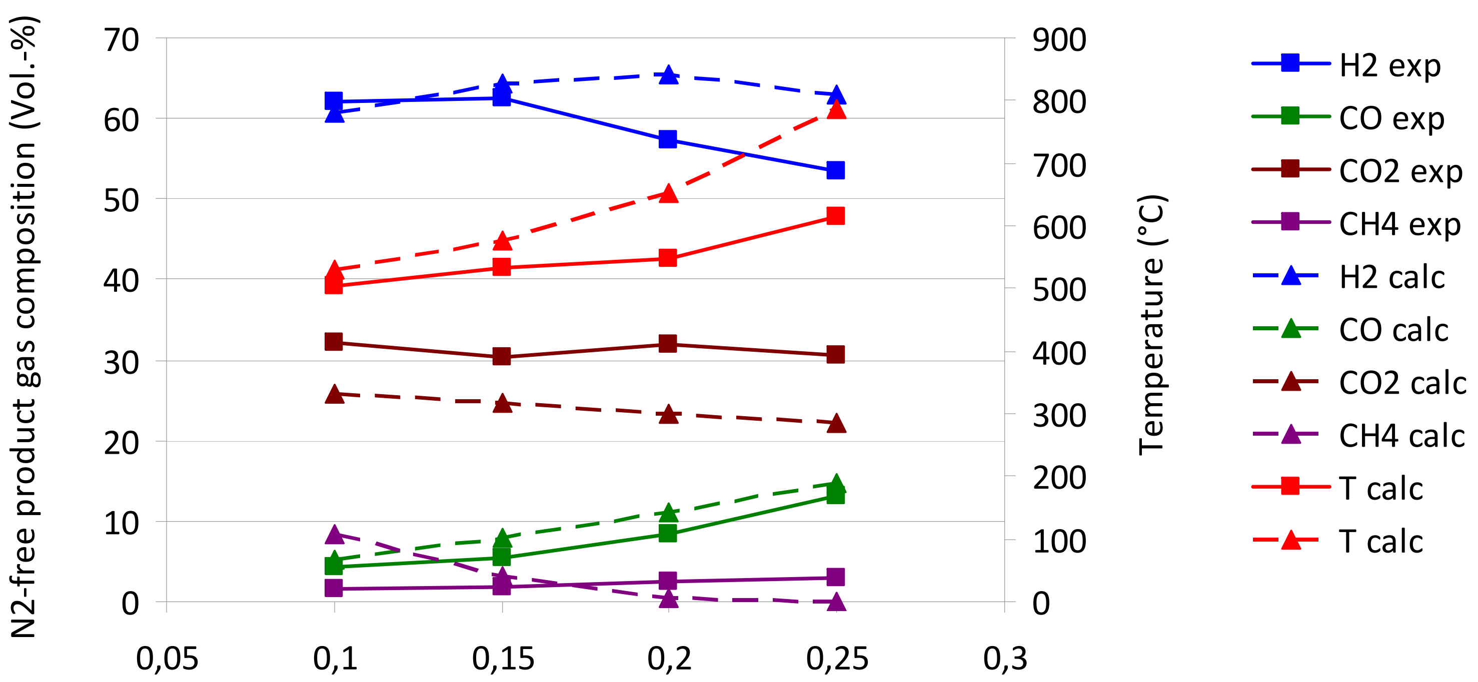
Simulation with Aspen Plus®

- Dry **reformate gas composition** (ATR Trioleate, S/C=3)



Simulation with Aspen Plus® II

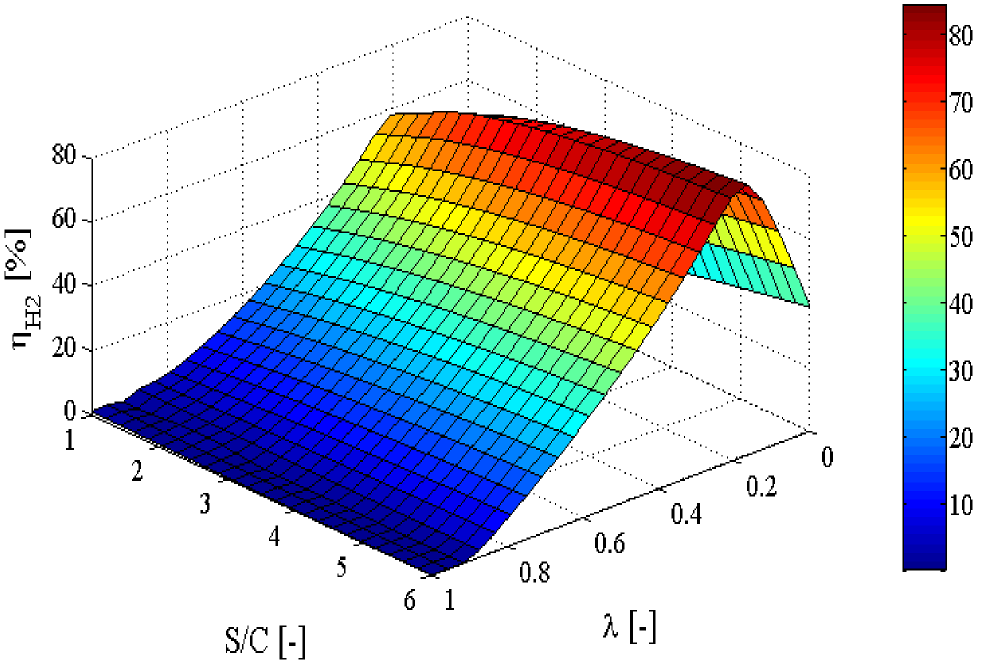
- Comparison between calculated and measured **dry product gas composition (nitrogen free basis**, S/C=3)



Simulation with Aspen Plus® III

$$\eta_{H2} = \frac{\dot{m}_{H_2}(t=0) \cdot H_{u,H_2}}{\dot{m}_{rapeseedoil} \cdot H_{u,rapeseedoil}}$$

- **Energetic efficiency η_{H2}** (ATR Trioleate, S/C: 1…6, λ: 0…1)

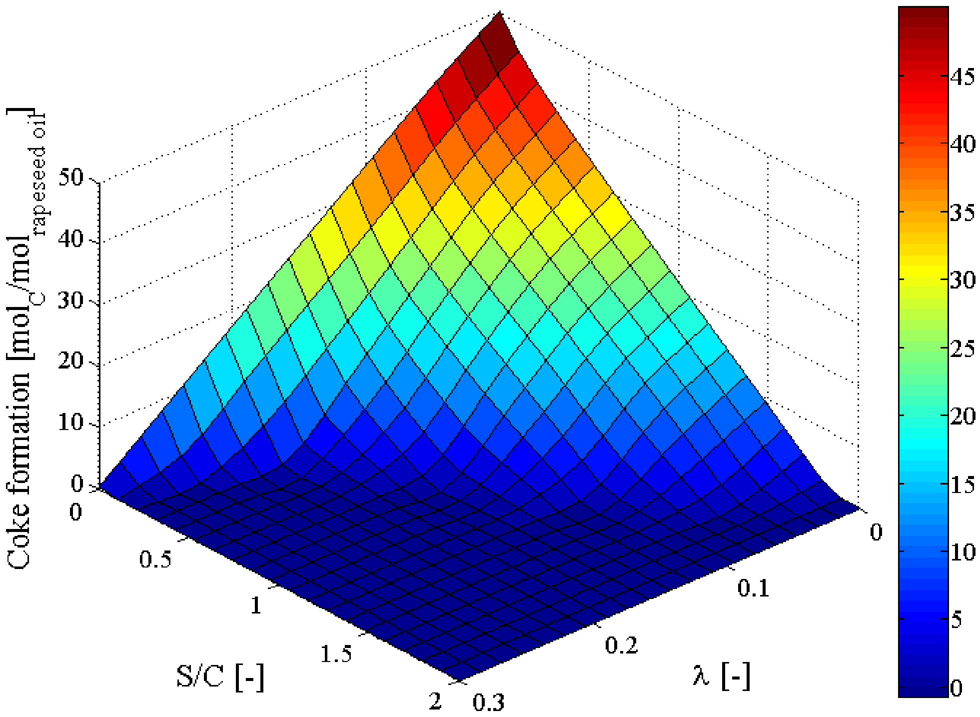


- Optimum curve for λ (at constant S/C)
- η_{H2}-maximum: 85% at λ=0,175
- Increasing η_{H2} with increasing S/C-ratio (at constant λ)

Practical experience: Kinetic limitations, catalyst deactivation, incomplete fuel conversion

Simulation with Aspen Plus® IV

- **Coking boundaries** (ATR Trioleate, S/C: 0…2, λ: 0…0,3)



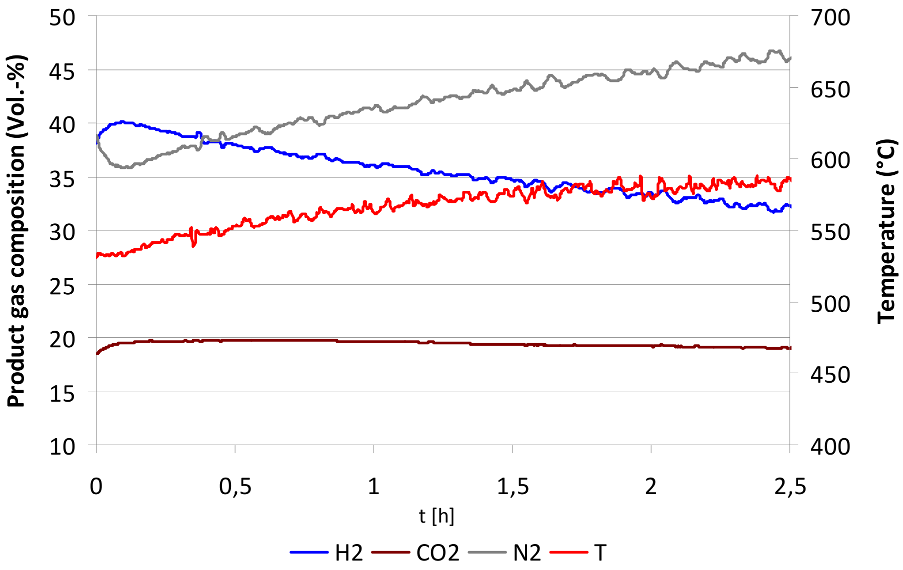
- Calculation of coking boundaries using Gibbs Minimization method
- Consideration of solid carbon (graphite) as possible product

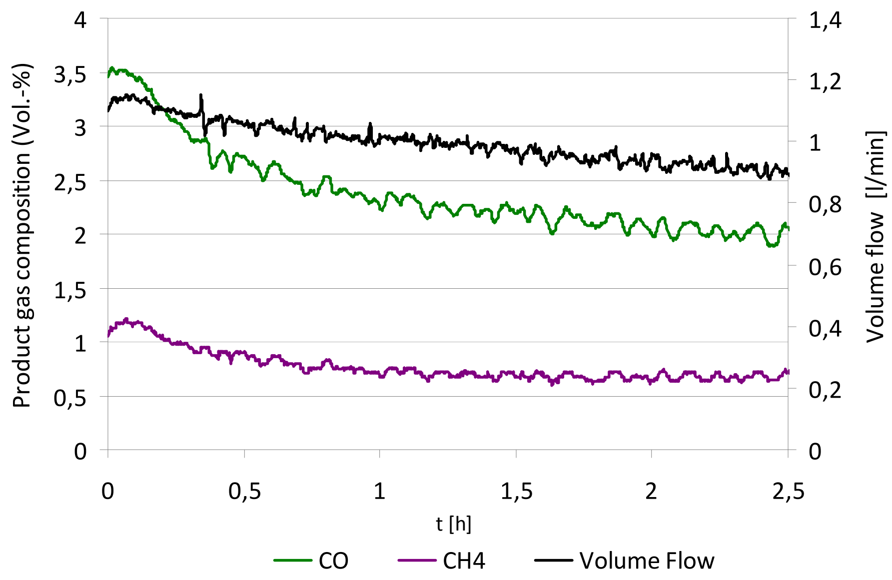
⇨ High coking rates at low S/C and low λ

Practical experience: Coking also occurs at higher S/C and λ (high temperatures)

Experimental Results

- **Reformate gas composition** (S/C=3, λ=0,15)

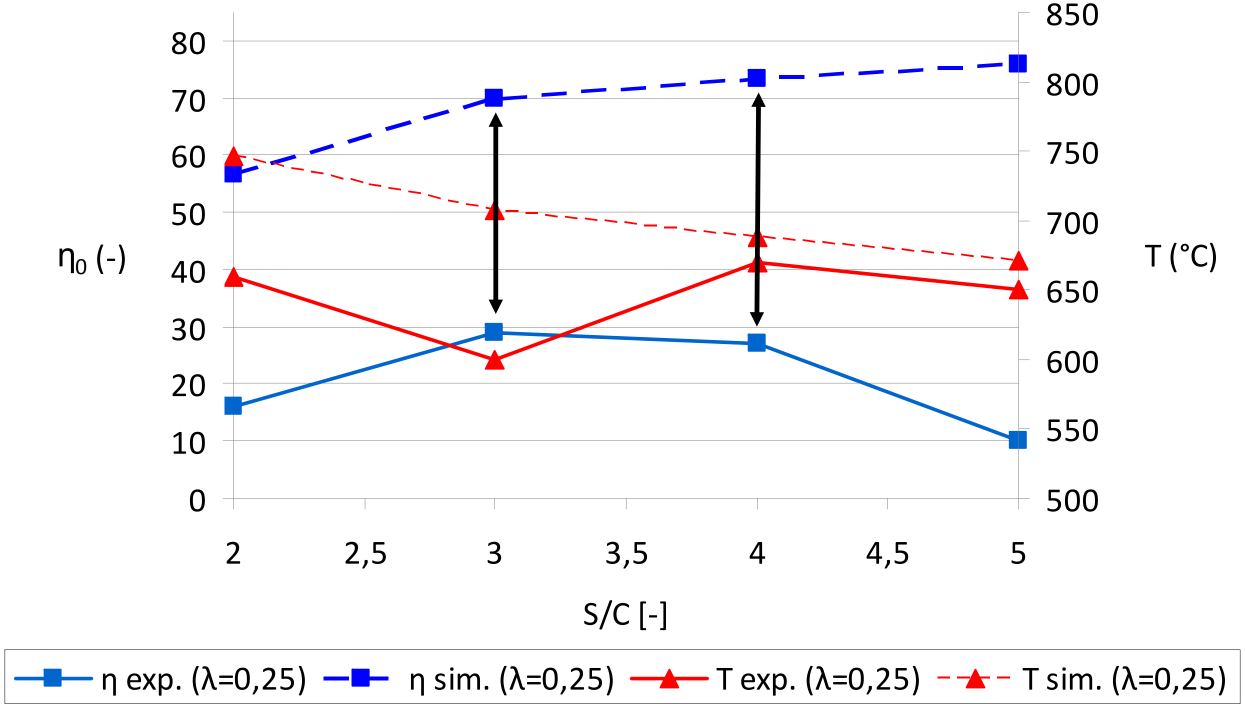




- H_2-concentration at t=0 lower than expected, decreasing continuously
- Catalyst deactivation with time → decrease of reformate volume flow, increase of product gas temperature
- H_2- and CO-concentration correlate

Experimental Results II

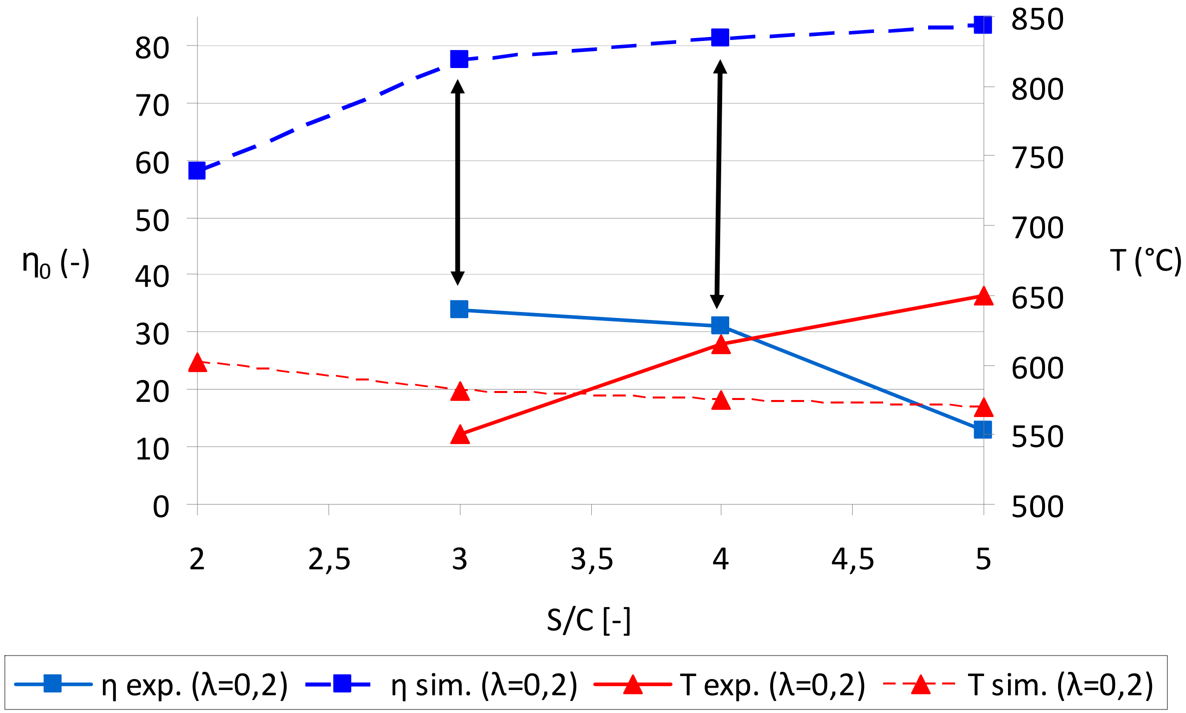
- **Variation of S/C** (*λ=0,25*)



- Optimum curve (maximum at S/C = 3)
- Measured efficiency η_0 lower than thermodynamic value
- Temperature lower than expected

Experimental Results II

Variation of S/C (*λ=0,20*)



Findings „Variation of S/C":

- Optimum curves (maximum at S/C = 3)

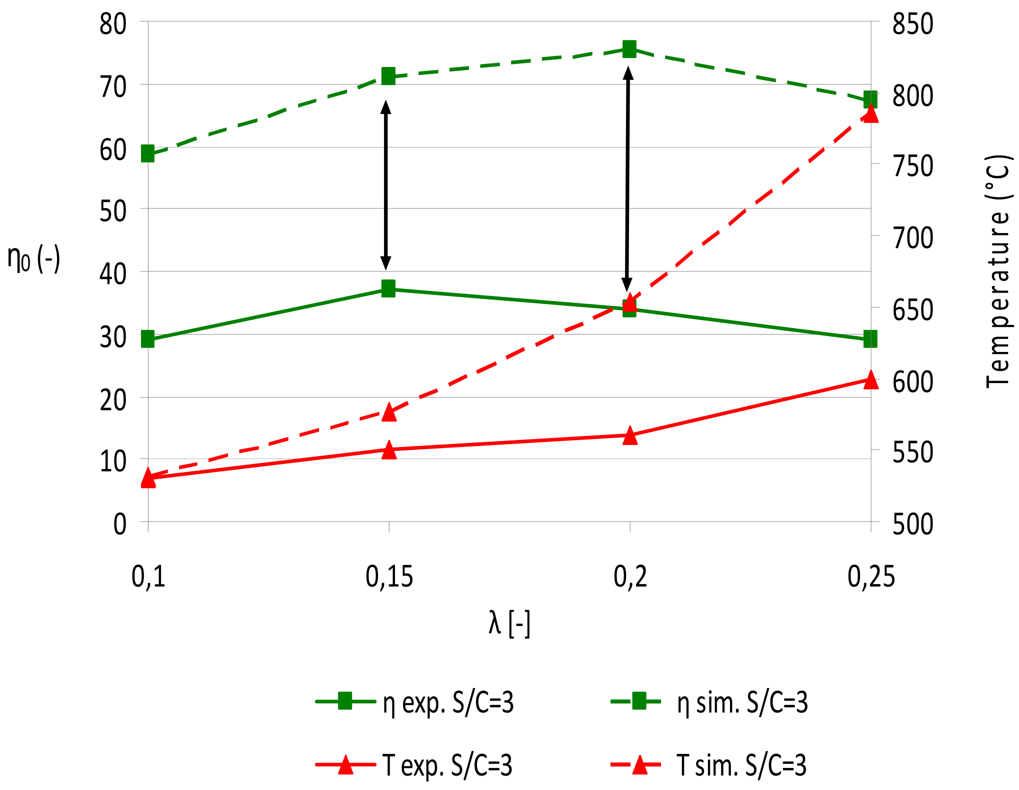
- S/C > 3: decrease of η_0
↔ thermodynamics: Higher η_0 at higher S/C

- S/C > 3: Temperature increase ↔ thermodynamics: Decrease of T with increasing S/C

Hypothesis: Kinetic Limitations
→ lower H_2 yield, less energy needed for reforming reactions
→ increase of temperature

Experimental Results III

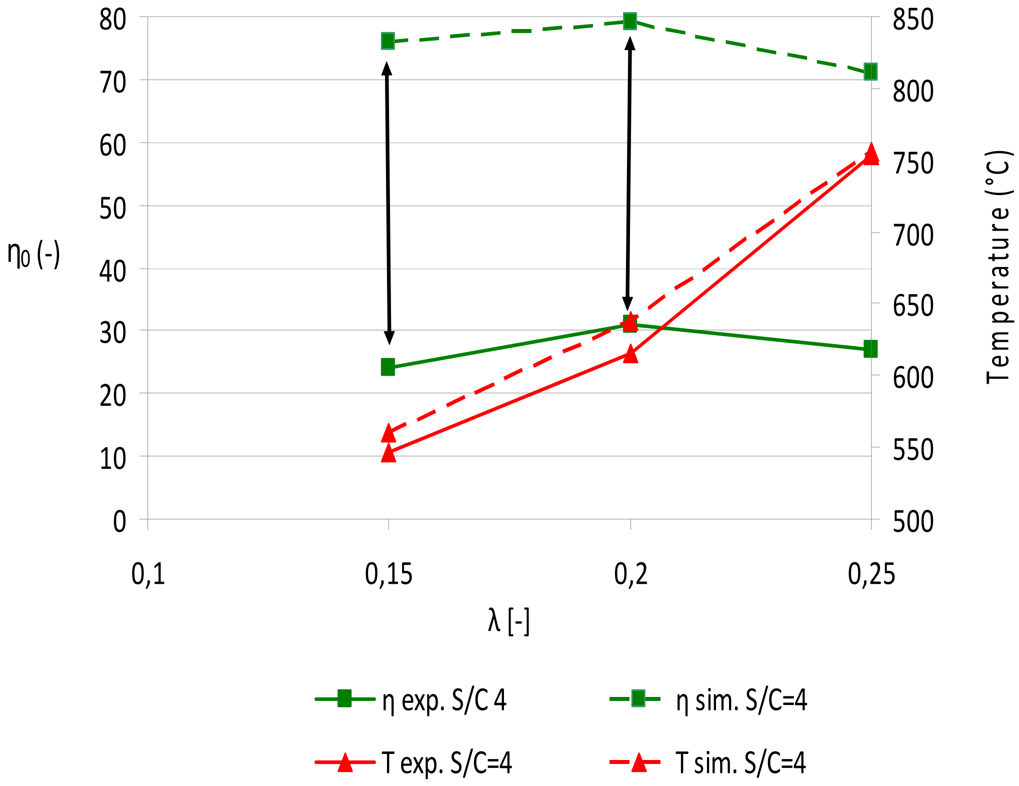
- **Variation of Air Ratio λ (*S/C=3*)**



- Optimum curve (maximum at λ = 0,15)
- Efficiency η_0 lower than thermodynamically predicted
- Temperature lower than expected

Experimental Results III

Variation of Air Ratio λ (*S/C=4*)



Findings „Variation of λ":

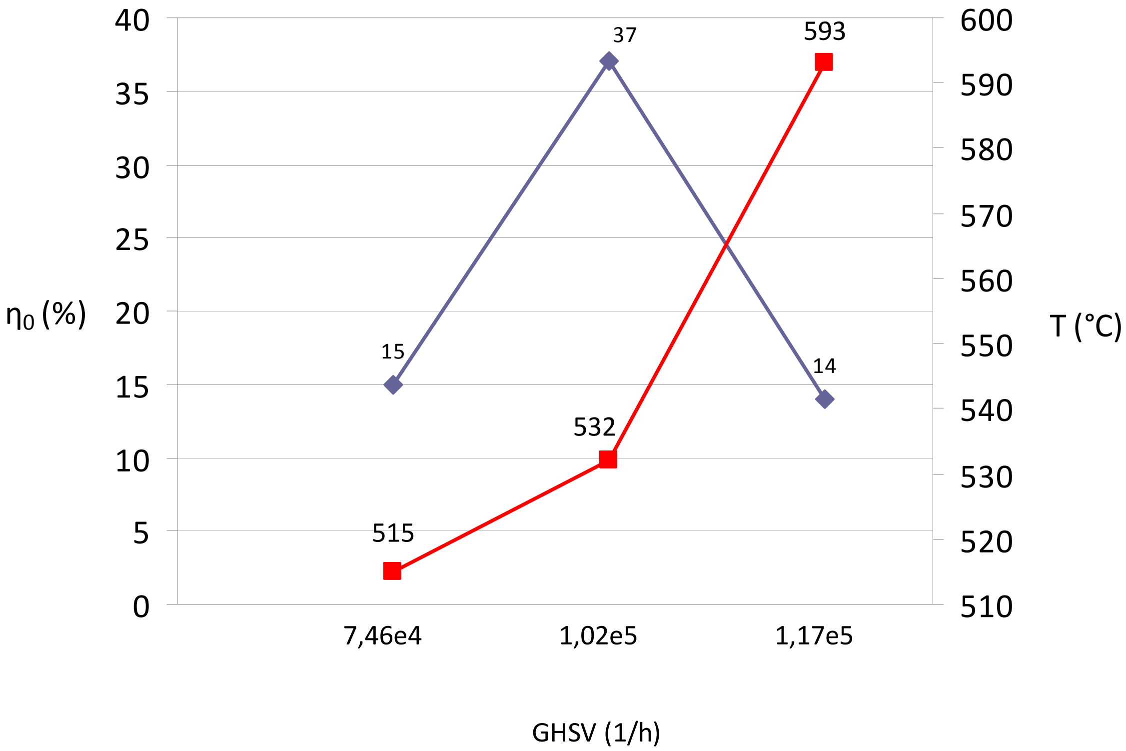
- Optimum curves (maximum at λ = 0,15/0,2)
- Trend of η_0 and T is similiar to thermodynamic predictions
- Calculated efficiency significantly lower than measured efficiency

⇩

Catalyst deactivation, incomplete fuel conversion…

Experimental Results IV

Variation of GHSV (S/C=3, λ=0,15)



- Optimum curve (maximum at GHSV = $1{,}02 \cdot 10^5$ 1/h)
- Lower GHSV: Effect of heat losses and coke formation
- Higher GHSV: Kinetic limations due to reduced reaction time

Experimental Results V

$$FC = 1 - \frac{\dot{m}_{cond.,organic}}{\dot{m}_{rapeseedoil}} \qquad CC = 1 - \frac{m_{C,reformate}}{\dot{m}_{C,rapeseedoil}}$$

- **Mass balance and Conversion rates** (Feed Conversion FC and Carbon Conversion CC)

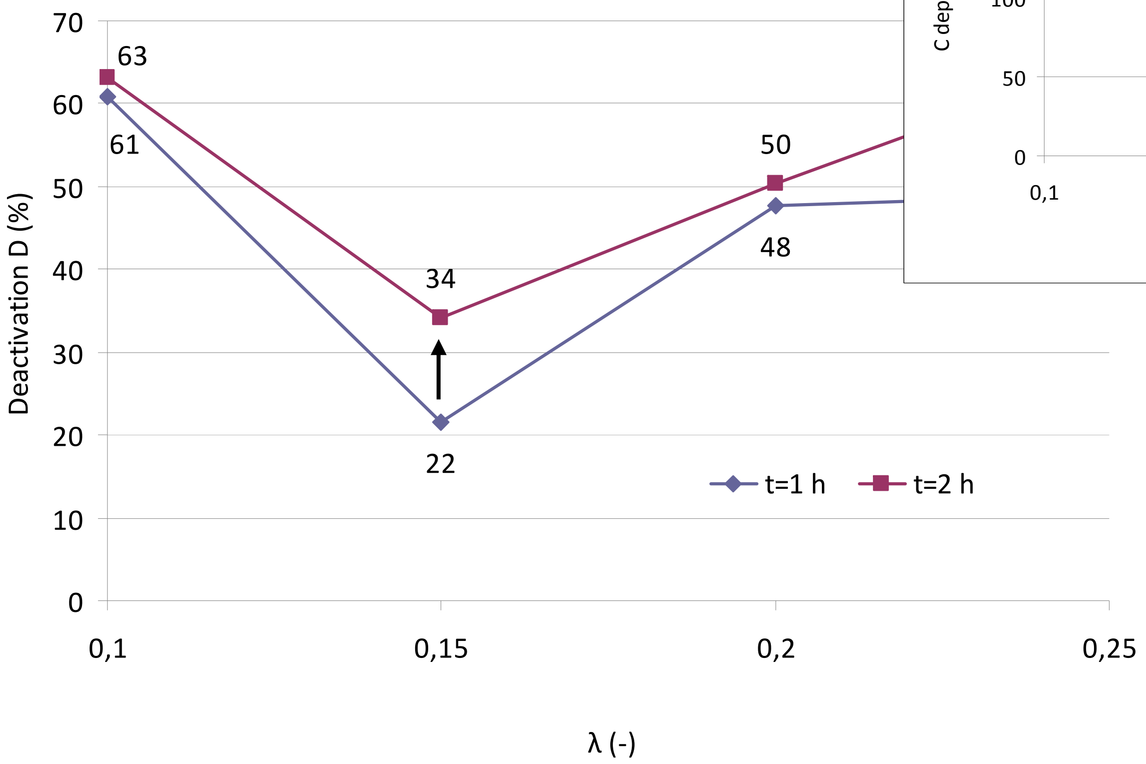
S/C (-)	λ (-)	mass balance inaccuracy (%)	FC (%)	CC (%)
3	0,1	15,3	88	33
3	0,15	17,5	83	49
3	0,2	27,4	93	48
3	0,25	19,7	89	56
4	0,15	22	83	26
4	0,2	25,8	87	54
4	0,25	9,3	97	55

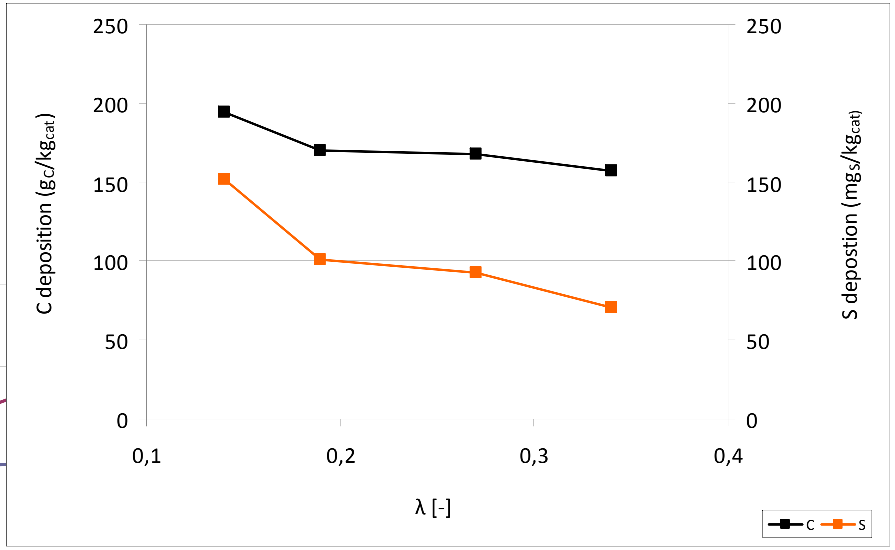
- Carbon conversion (CC) significantly lower than Fuel Conversion (FC)

  ⇒ Coke deposition on catalyst and inside tubings + formation of higher HCs?

Experimental Results VI

- Catalyst deactivation





- Deactivation Minimum at λ_{opt}=0,15
- Continuous decrease of C- and S-deposition with increasing λ

Further deactivation mechanisms!

Summary

- Alternative option for „green“ hydrogen production: Reforming of liquid biofuels
- Rapeseed oil especially advantageous from an ecological and economical point of view
- S. Martin et al. (2011): 6-8 % of the actual fuel consumption could theoretically be covered by hydrogen from rapeseed oil in Germany in the year 2020
- Simulation results with Aspen Plus: Process efficiency of higher than 80 % can be achieved
- Experiments proved feasibility of hydrogen production from rapeseed oil
- Influence of S/C, λ and GHSV was investigated in detail. → Efficiency is significantly lower that thermodynamically predicted due to incomplete fuel conversion and catalyst deactivation
- Catalyst deactivation cannot be solely attributed to coking and/or sulphur poisoning!
- Next Steps: Investigate reasons for catalyst deactivation, enhance fuel conversion, catalyst development

Thank you for your attention!

Research Group „Alternative Fuels“

Antje Wörner (Antje.Woerner@dlr.de)

Tel.: +49 711-6862-484

Lecturer: Stefan Martin (Stefan.Martin@dlr.de)

Tel.: +49 711-6862-682