Karlsruhe Institute of Technology

bioliq
Biomass to Liquid Karlsruhe

# Operations of the bioliq® pilot plant - entrained flow gasification in 5 MW pilot scale

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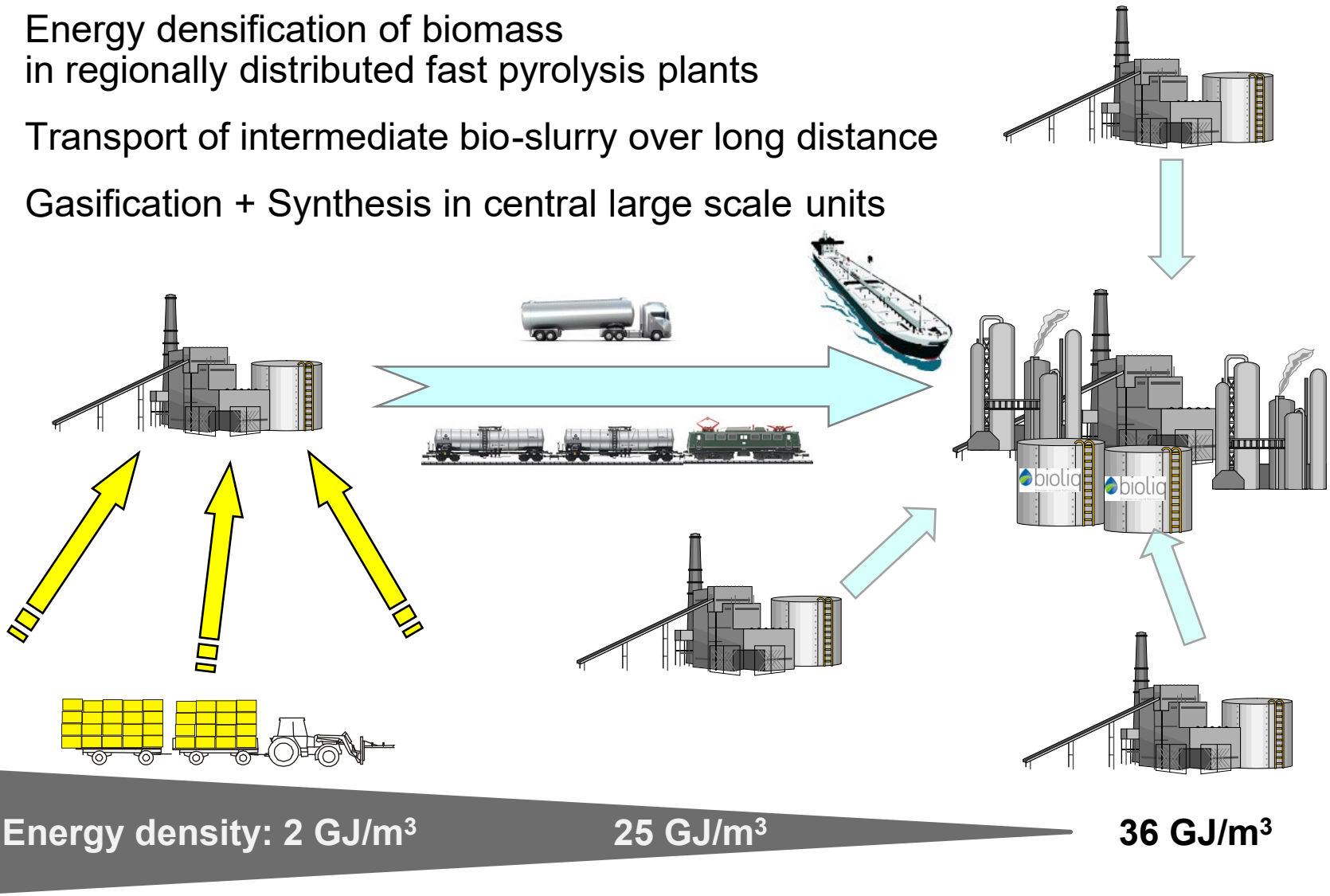
Waste2H2 - Workshop, KIT, September 19-26, 2022

bioliq biomass to liquid

Institute for Technical Chemistry, ITC
Institute for Catalysis Research and -Technologie, IKFT
Engler-Bunte-Institute, Fuel Technology, EBI ceb

# bioliq® de-central / central concept

- Energy densification of biomass
  in regionally distributed fast pyrolysis plants
- Transport of intermediate bio-slurry over long distance
- Gasification + Synthesis in central large scale units



# bioliq® pilot plant

Gefördert durch:
Bundesministerium für Ernährung und Landwirtschaft
aufgrund eines Beschlusses des Deutschen Bundestages
FNR Fachagentur Nachwachsende Rohstoffe e.V.

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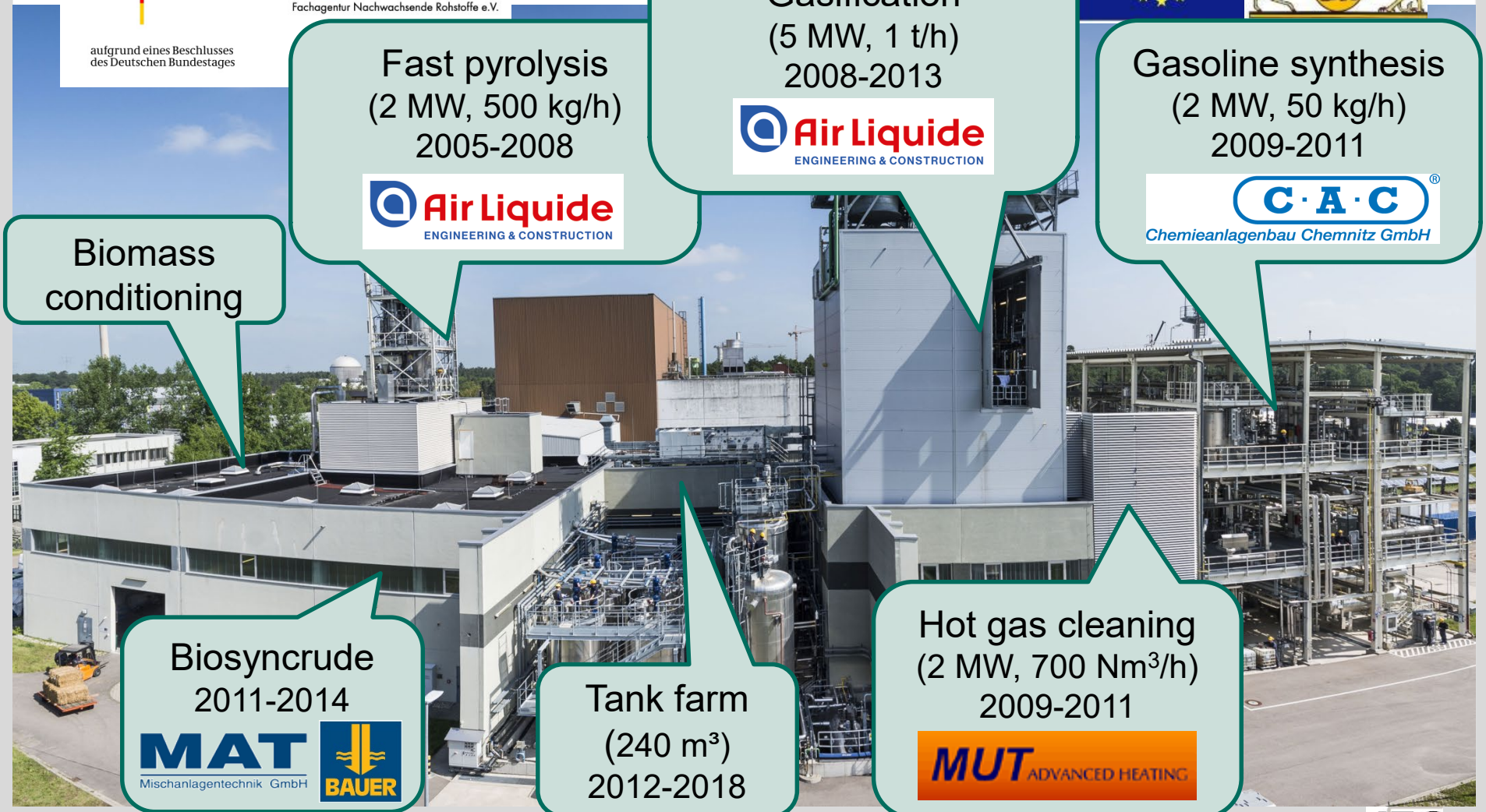
KIT Karlsruhe Institute of Technology



Biomass conditioning

Fast pyrolysis
(2 MW, 500 kg/h)
2005-2008
Air Liquide ENGINEERING & CONSTRUCTION

High Pressure Entrained Flow Gasification
(5 MW, 1 t/h)
2008-2013
Air Liquide ENGINEERING & CONSTRUCTION

Gasoline synthesis
(2 MW, 50 kg/h)
2009-2011
C·A·C Chemieanlagenbau Chemnitz GmbH

Biosyncrude
2011-2014
MAT Mischanlagentechnik GmbH
BAUER

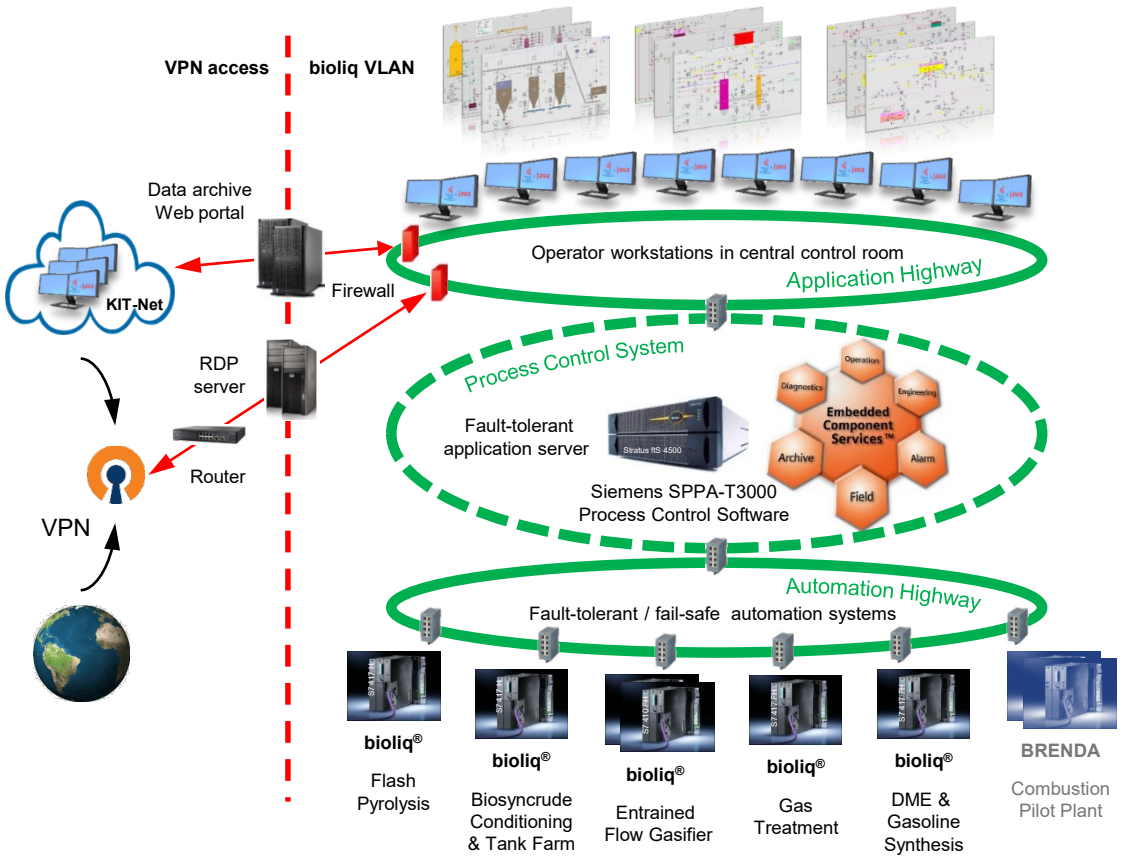
Tank farm
(240 m³)
2012-2018

Hot gas cleaning
(2 MW, 700 Nm³/h)
2009-2011
MUT ADVANCED HEATING

# bioliq® pilot plant

- Designed as pilot plant with many options concerning R&D for process optimization, not as a production plant
- Operated in 4 to 5 campaigns per year, each with 2-5 weeks of 24/7 operation
- Operated by a staff of about 40 operators and engineers in a 4-shift system

# bioliq® - Process Control System (PCS)

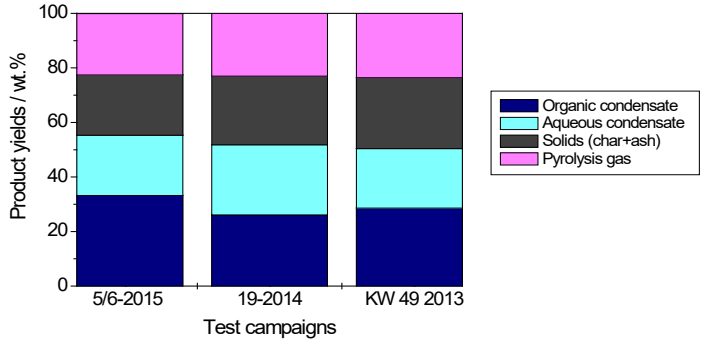


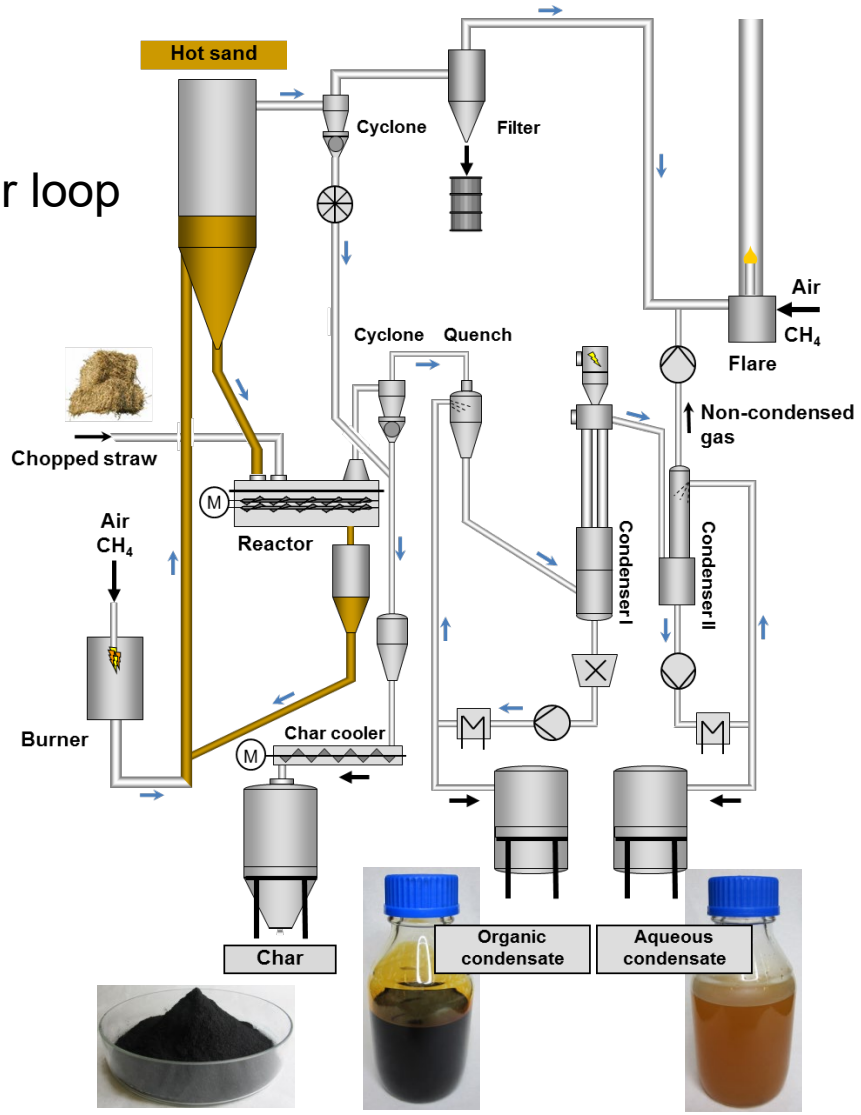

## Features

- Process control software Siemens SPPA -T3000
- Fault-tolerant / fail-safe automation systems Simatic S7 400 series
- PROFIBUS connectivity to approximately 20 sub-systems
- Extensive instrumentation, in total:
  - ~ 200 electrical drives
  - ~ 350 shut-off valves
  - ~ 2000 measured variables
  - ~ 2400 alarms and warnings
  - ~ 250 PID control loops
  - ~ 150 SIL 1 & SIL 2 safety functions
- Fulfills operation requirements for:
  - explosion protection zones
  - functional safety acc. to IEC 61508
- 8 Operator workstations in central control room
- Secured external data access through Virtual Private Network (VPN) and Remote Desktop Protocol (RDP)

# bioliq® - fast pyrolysis

- Main features (feed wheat straw)
  - Twin screw mixer reactor (500 °C)
  - Heat transfer by sand in a heat carrier loop
  - Gas retention time ~ 1-2 sec
  - Two-stage condensation (~ 90 °C / ~ 30 °C)
- Main products
  - Straw char ($d_{90}$ < 100 µm)
  - Organic condensate
  - Aqueous condensate

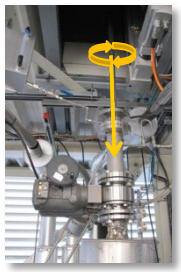


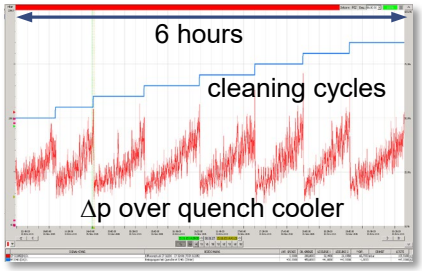



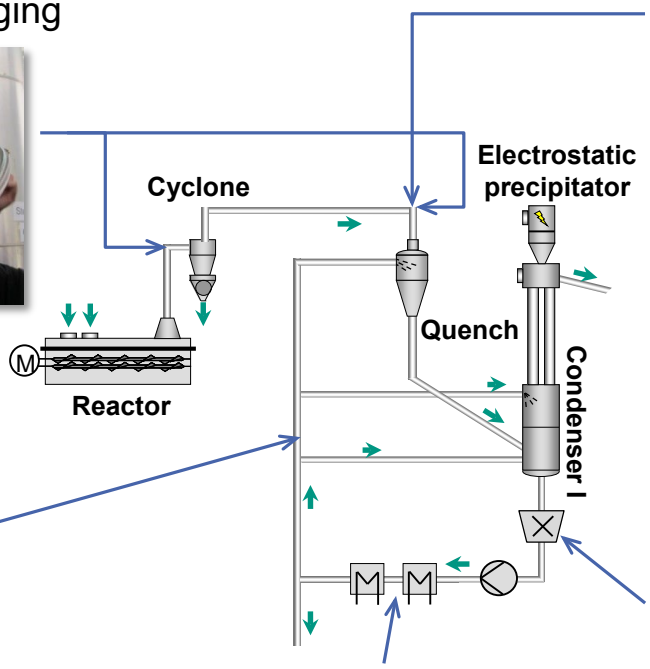
# bioliq® - fast pyrolysis

## Optimization of organic condensate loop

- Acoustic system for pipe cleaning
  ⇒ prevents pipes from clogging

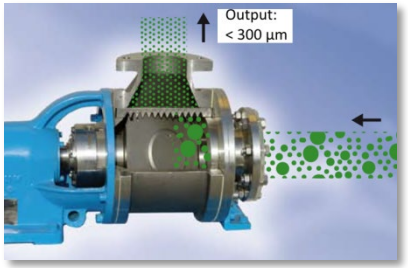




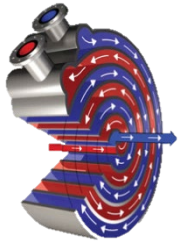

- Automated mechanical cleaning unit
  ⇒ removes caking deposits
  ⇒ avoids critical pressure drops

| Properties organic condensate (OC) | | |
|---|---|---|
| HHV | MJ/kg | ≈ 20 |
| Water | wt.% | 10-20 |
| Solids | wt.% | < 10 |
| Density | kg/m³ | ≈1200 |




*Pictures by hoelschertechnic-gorator®*

- Two spiral heat exchangers
  ⇒ avoids fouling by viscous, solid containing bio-oil ("self cleaning")



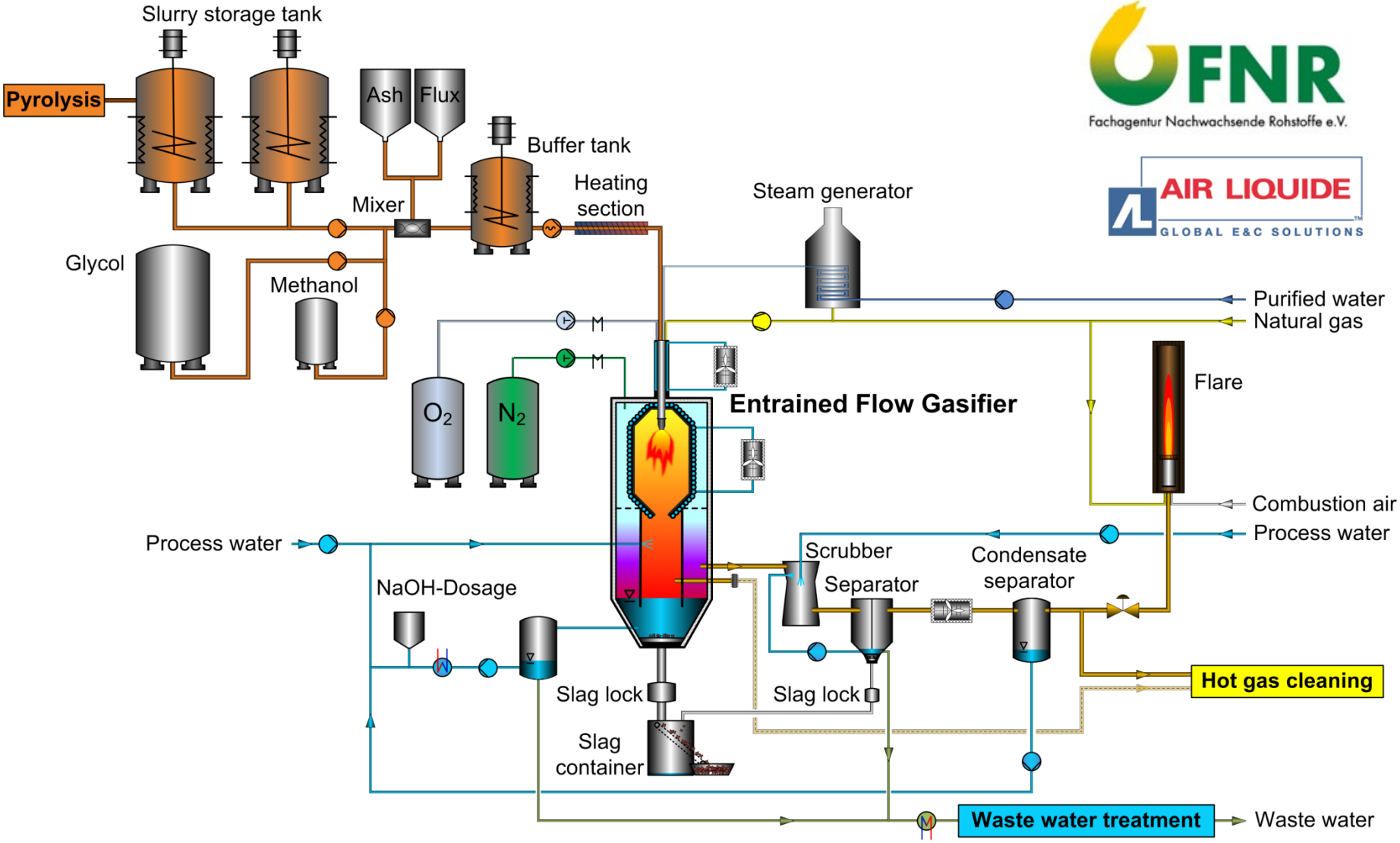
*Picture by Alfa Laval*

- Macerator keeps solids < 300 $\mu m$
  ⇒ prevents blockages in quench nozzles and piping

# bioliq® - fast pyrolysis, status quo

- Stable operation and representative product yield since 2015
  - Substantial increase of straw throughput per week from < 5 t in 2012 up to > 40 t in 2018
  - > 260 t of wheat straw processed
- Feedstock flexibility was proven in campaigns > 18 t of miscanthus
- Organic condensate with remaining solids, can be used in the bioliq® gasifier without further treatment
- Biosyncrude from aqueous condensate & straw char is being qualified as a fuel for the entrained flow gasifier

# bioliq® - entrained flow gasifier (EFG)



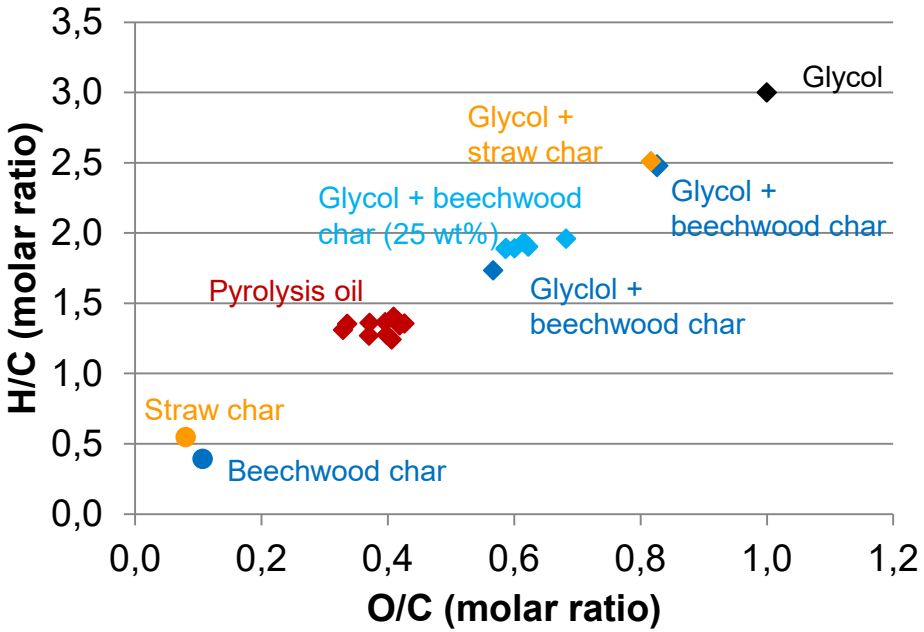
# bioliq® - EFG, fuel specification

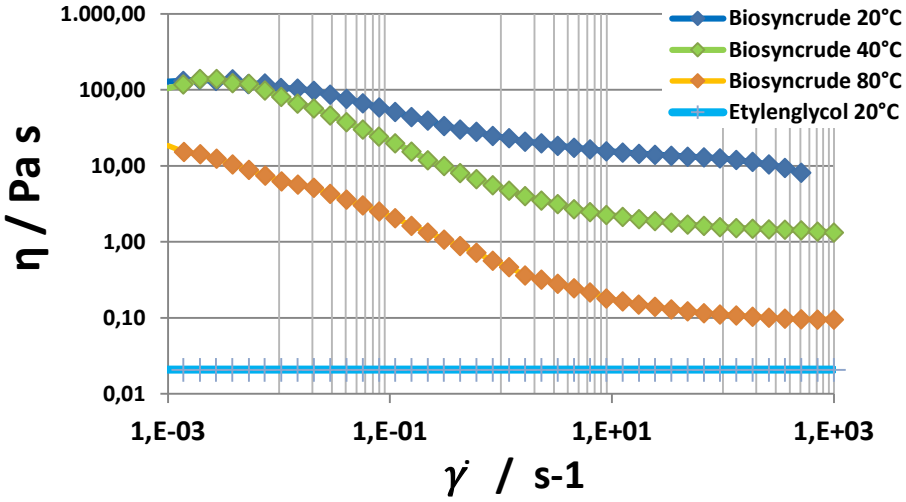
## *Liquid Phase:*

- Glycol as surrogate / model fuel
- BioSyncrude: straw based pyrolysis oil
- Wood based pyrolysis oil

## *Solid phase:*

- Coke: Straw and wood based
- Ash: straw / glass



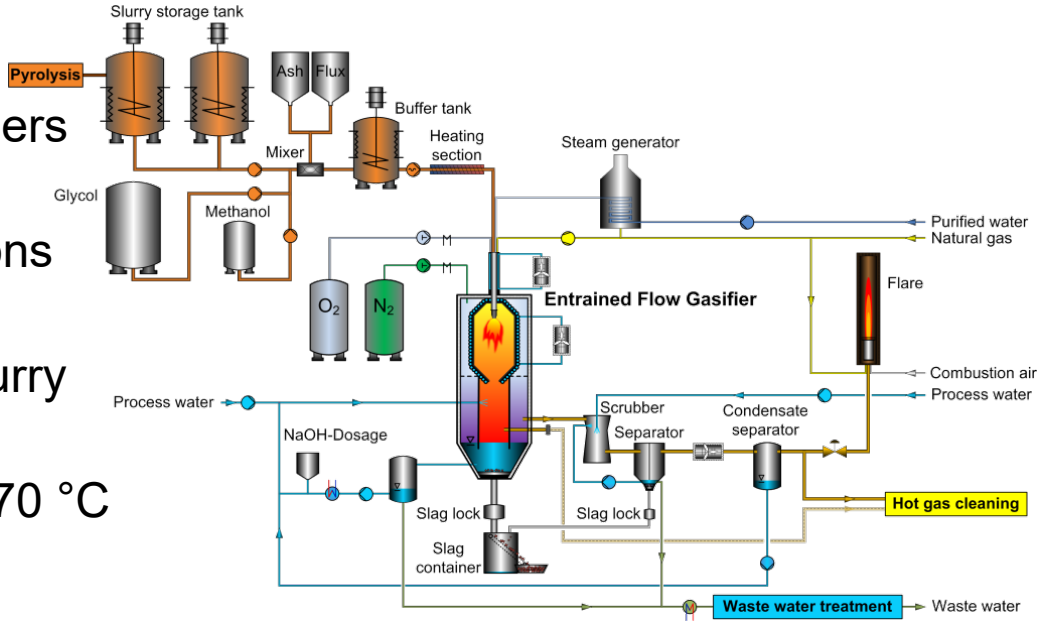




## *Fuel specification:*

- LCV 13 – 25 MJ/kg
- Solid content < 30 %wt
- Ash content 3 - 10 %wt
- $d_p$ 90 % < 100 µm / max 1 mm
- Viscosity < 1 Pas (70°C)

# bioliq® - entrained flow gasifier (EFG)

- Main features
  - Two membrane walls and burners for operation at 40 bar / 80 bar
  - Alternative quench configurations (dip tube / spray quench)
  - Load range 700 - 1000 kg/h slurry (LHV 13 - 25 MJ/kg)
  - Slurry viscosity up to 1 Pas at 70 °C
  - Special equipment for R&D:
    - Optical access to reaction chamber
    - Sequential cooling in membrane walls (5 segments)
    - Extensive instrumentation & sampling possibilities for complete mass, species and energy balances

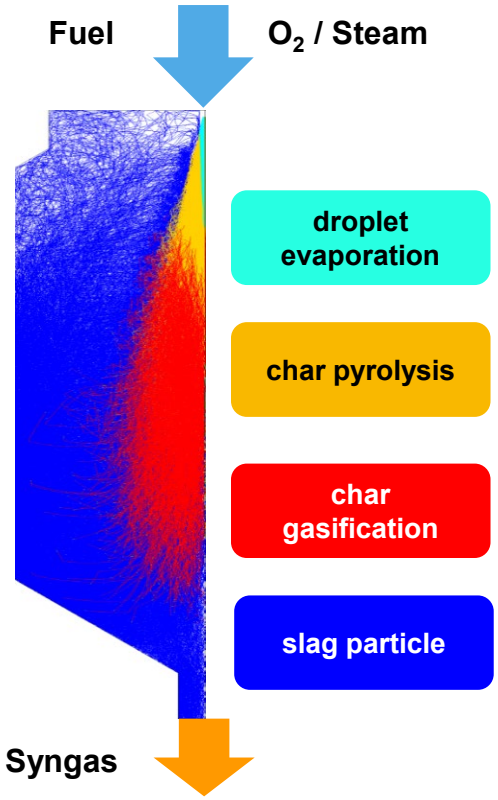



- Typical syngas composition (vol.%, dry)

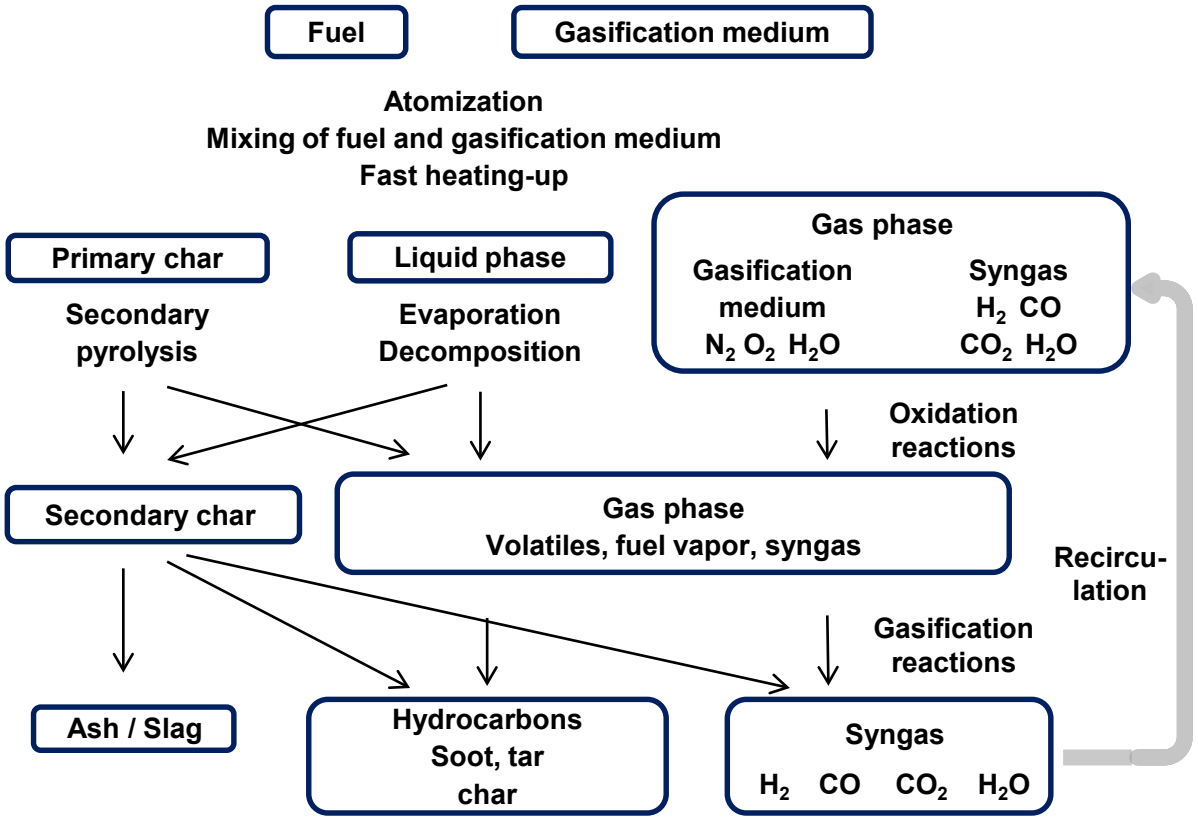
| $H_2$ | CO | $CO_2$ | $N_2$ | $CH_4$ |
|---|---|---|---|---|
| 28 - 33 | 28 - 37 | 18 - 27 | 12 - 18 | < 0.1 - 0.3 |

# bioliq® - EFG

## Sub-processes – conversion of suspension fuels

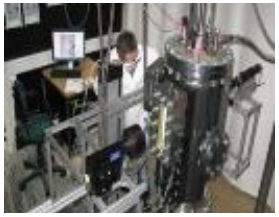



RANS: TU Clausthal / IEVB



# bioliq® - EFG, integrated research approach

### High Pressure Atomization

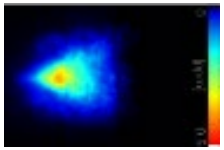


PAT

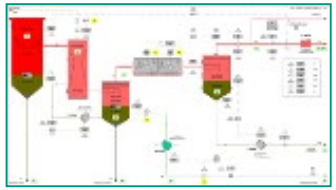
### Entrained Flow Gasification

REGA

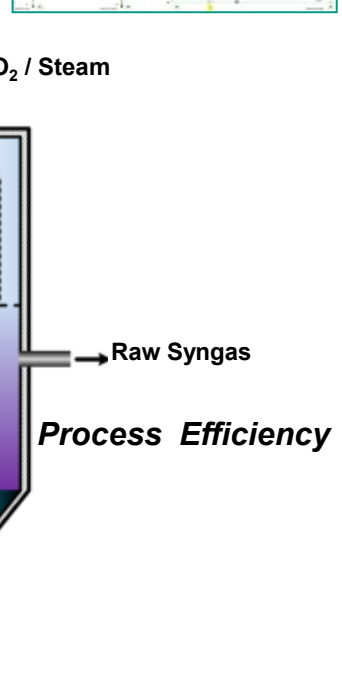
### Measuring Techniques



### Slag Control

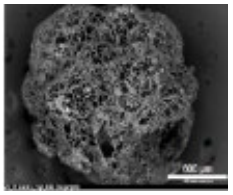


### Process Control

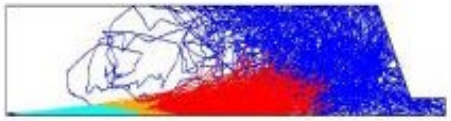



### Process Efficiency

### Fuel Conversion



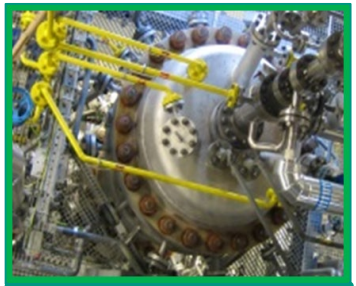
### Numerical Simulation



### bioliq® EFG

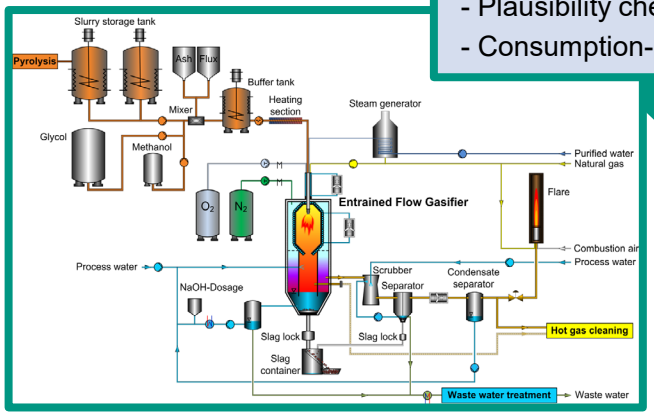
5MW
80 bar

# bioliq® - EFG, balancing tools

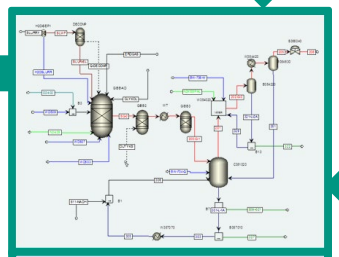


**EFG – pilot plant**
- PLS Siemens T3000
- THETIS web-Portal
- Excel-Interface

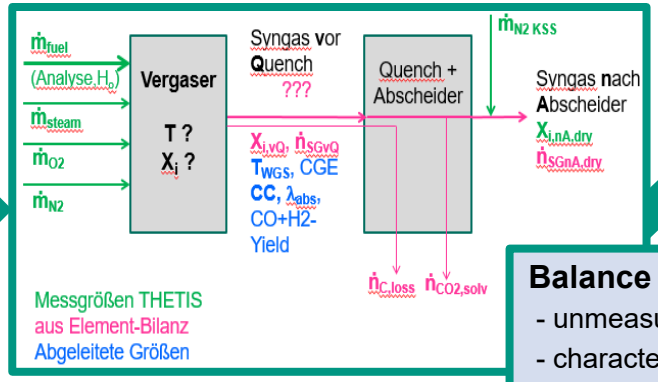
**~ 500 raw data**




**Balance bioliq - EFG process**
- Plausibility check of measured values
- Consumption- / emission data



**ASPEN-Model**
(stationary)

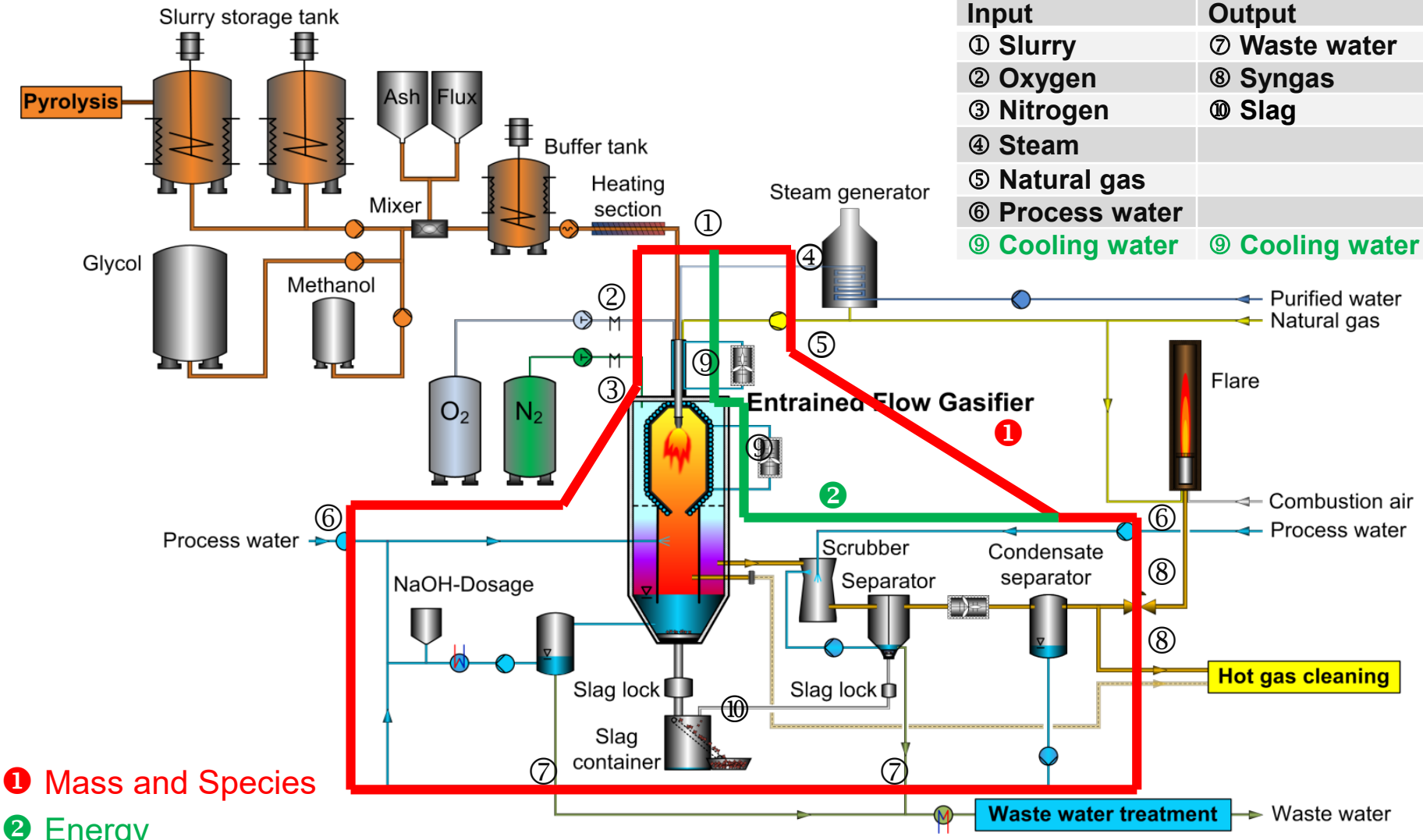



**Validated Database**

**Balance bioliq - EFG reactor**
- unmeasured parameters
- characteristic indicators / numbers
- Plausibility check of measured values

# bioliq® - EFG, balances

| Input | Output |
|---|---|
| ① Slurry | ⑦ Waste water |
| ② Oxygen | ⑧ Syngas |
| ③ Nitrogen | ⑩ Slag |
| ④ Steam | |
| ⑤ Natural gas | |
| ⑥ Process water | |
| ⑨ Cooling water | ⑨ Cooling water |

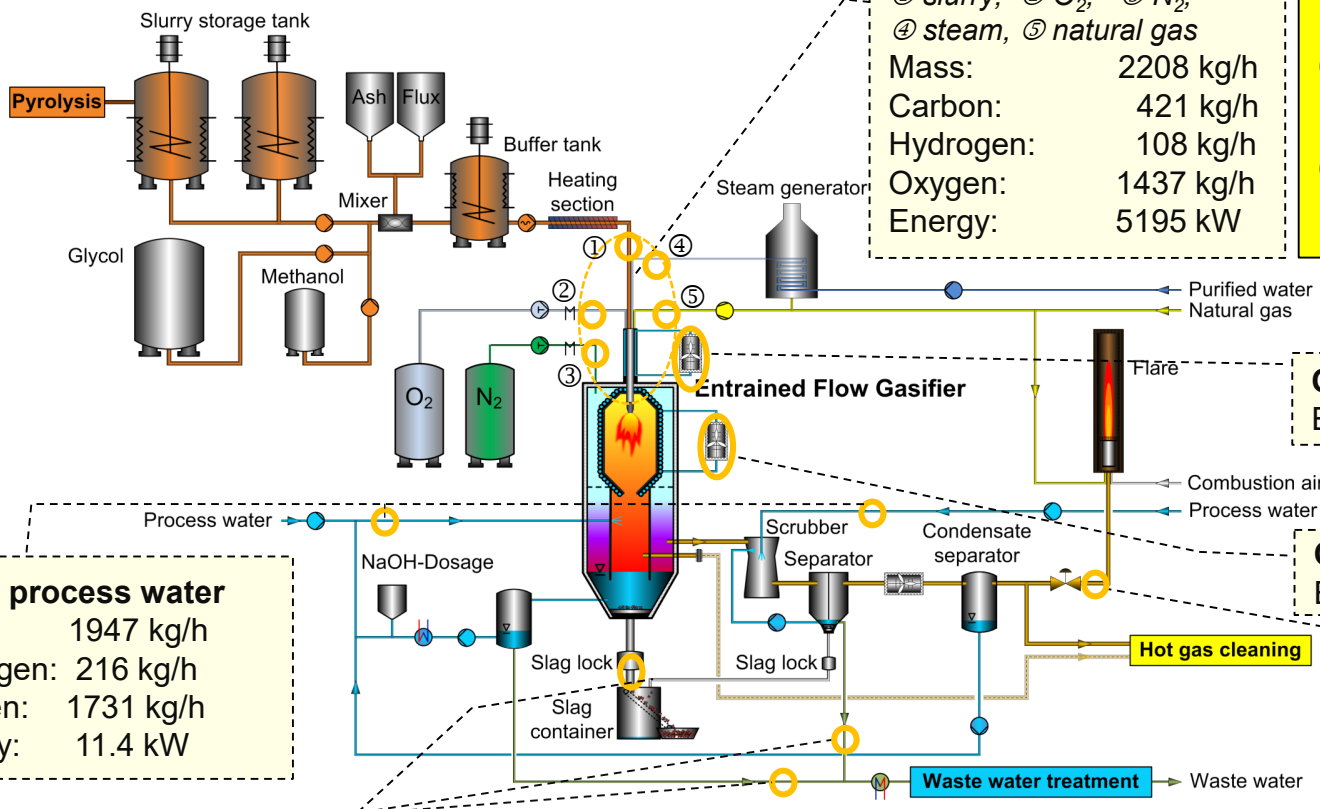



❶ Mass and Species

❷ Energy

# bioliq® - EFG, balances

Experiment: **V26;** 7.42 h
Slurry 34: MEG + 25% wood coke + 5% straw ash; (767.9 kg/h)




**Input**:
① *slurry*, ② $O_2$, ③ $N_2$,
④ *steam*, ⑤ *natural gas*

| | |
|---|---|
| Mass: | 2208 kg/h |
| Carbon: | 421 kg/h |
| Hydrogen: | 108 kg/h |
| Oxygen: | 1437 kg/h |
| Energy: | 5195 kW |

**Balances:**

| | |
|---|---|
| Mass: | 97.0 % |
| Carbon: | 102.9 % |
| Hydrogen: | 96.2 % |
| Oxygen: | 96.0 % |
| Energy: | 98.5 % |

**Output: burner cooling**
Energy: 12.3 kW

**Output: cooling screen**
Energy: 741 kW

**Input: process water**

| | |
|---|---|
| Mass: | 1947 kg/h |
| Hydrogen: | 216 kg/h |
| Oxygen: | 1731 kg/h |
| Energy: | 11.4 kW |

**Output: waste water**

| | |
|---|---|
| Mass: | 2430 kg/h |
| Hydrogen: | 269 kg/h |
| Oxygen: | 21690 kg/h |
| Energy: | 106.3 kW |
| (Slag: | 30 kg/h) |

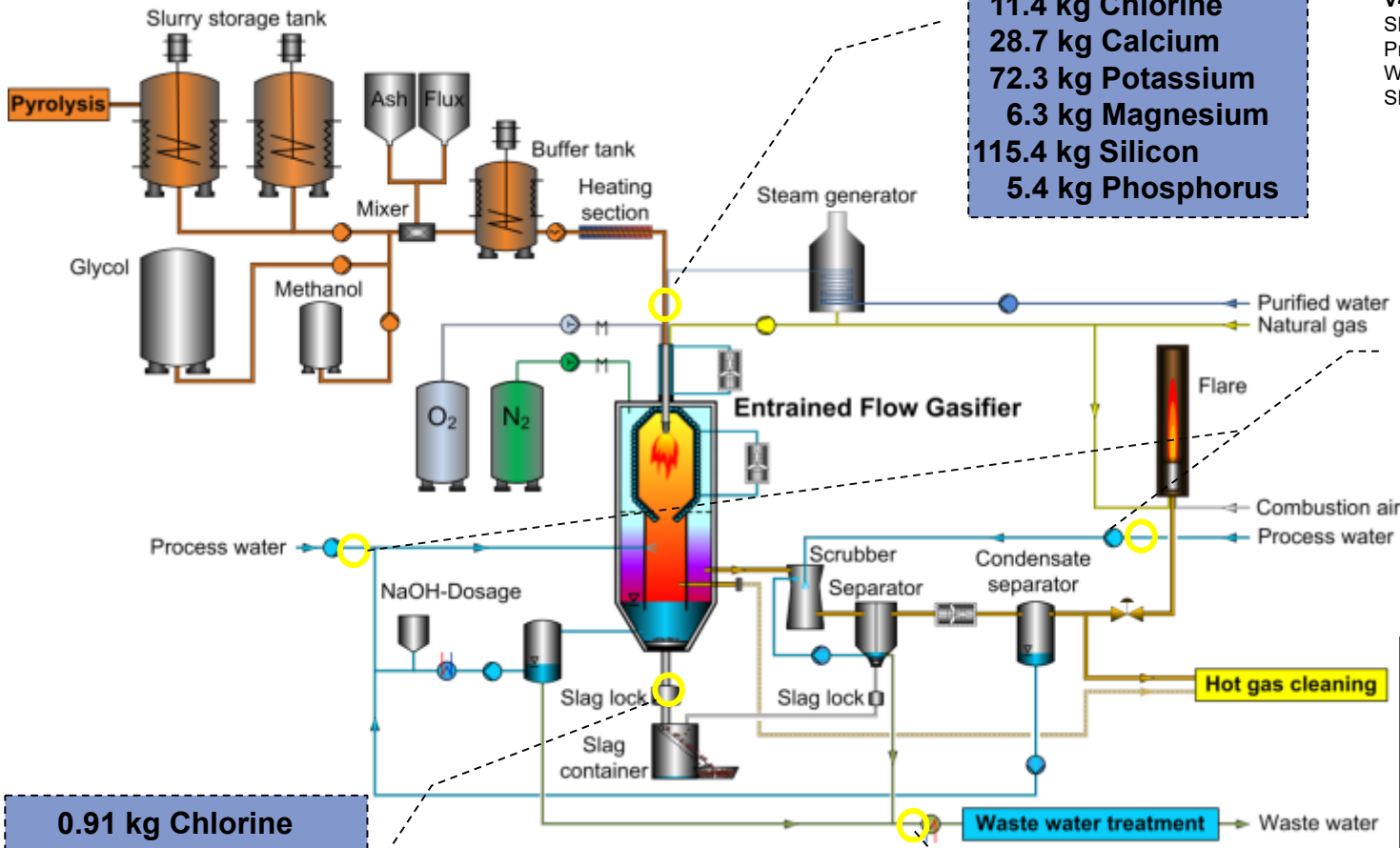
**Output:**

| | |
|---|---|
| Waste heat syngas cooling: | 48.8 kW |
| Waste heat quench: | 1141 kW |
| Heat loss reactor surface: | 50 kW |

**Output: syngas**

| | |
|---|---|
| Mass: | 1568.5 kg/h |
| Carbon: | 433 kg/h |
| Hydrogen: | 43 kg/h |
| Oxygen: | 882 kg/h |
| Energy: | 2882.5 kW |

# bioliq® - EFG, balance inorganics




**11.4 kg Chlorine**
**28.7 kg Calcium**
**72.3 kg Potassium**
**6.3 kg Magnesium**
**115.4 kg Silicon**
**5.4 kg Phosphorus**

**V43**, 15,67h
Slurry 53: 848,84 kg/h; 3,6 % Ash
Process water: 1151,47 kg/h
Waste water: 1654,9 kg/h
Slag: 375 kg

**0.65 kg Chlorine**
**2.11 kg Calcium**
**0.07 kg Potassium**
**0.27 kg Magnesium**
**0.0974 kg Silicon**
**0.0018 kg Phosphorus**

**0.91 kg Chlorine**
**25.78 kg Calcium**
**54.14 kg Potassium**
**5.93 kg Magnesium**
**108.70 kg Silicon**
**4.58 kg Phosphorus**

**9.91 kg Chlorine**
**2.54 kg Calcium**
**22.63 kg Potassium**
**1.01 kg Magnesium**
**5.57 kg Silicon**
**0.0164 kg Phosphorus**

**Balances:**

| | |
|---|---|
| Slag/Ash: | 78.3 % |
| Cl: | 90.0 % |
| Ca: | 91.8 % |
| K: | 106.1 % |
| Mg: | 106.0 % |
| Si: | 98.9 % |
| P: | 89.4 % |

# bioliq® - EFG, simulation tools

Develop simulation tools / guidelines for

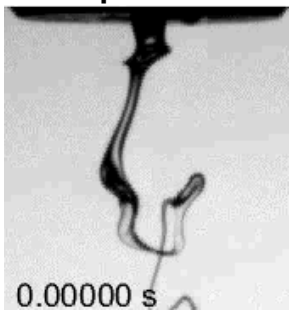
- Adaption of process parameters to varying fuel specifications
- Optimization of gasifier operation

Burner stability
Char conversion
Slag flow

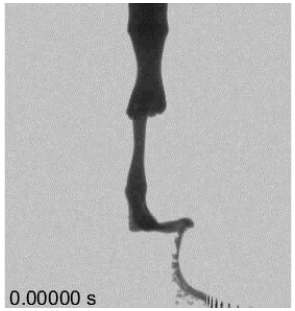
Cold gas efficiency
Syngas quality
Turn-down ratio

## Virtual Spray Test Rig

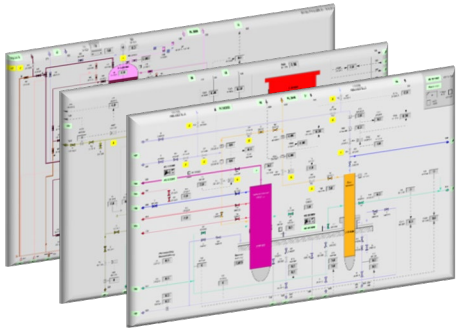
**Experiment**



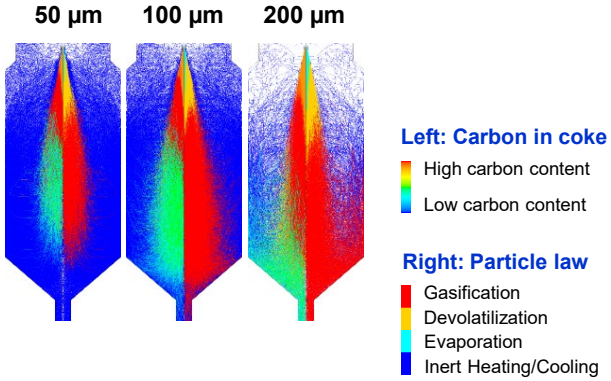

**Simulation**




## Digital Twin EFG

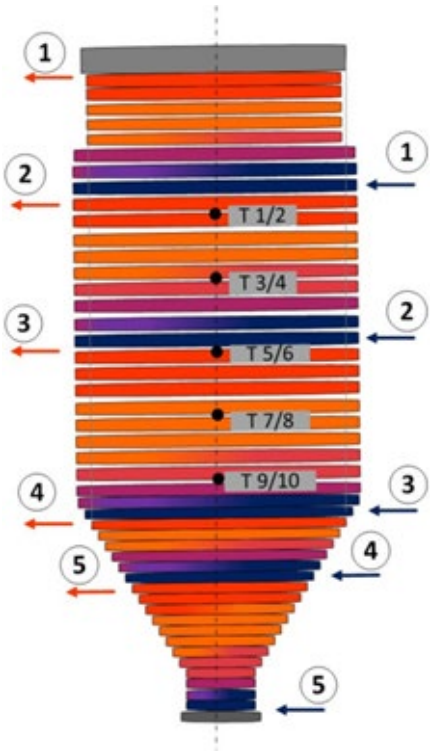


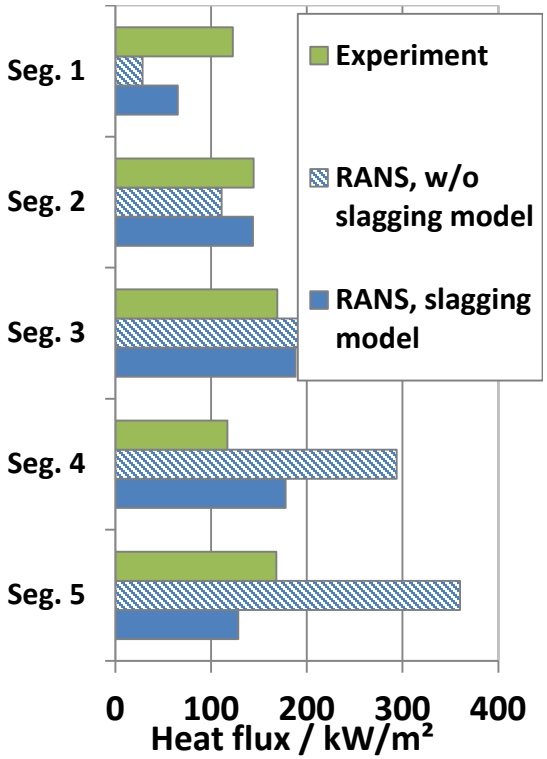
## Design Spec Simulation Tool

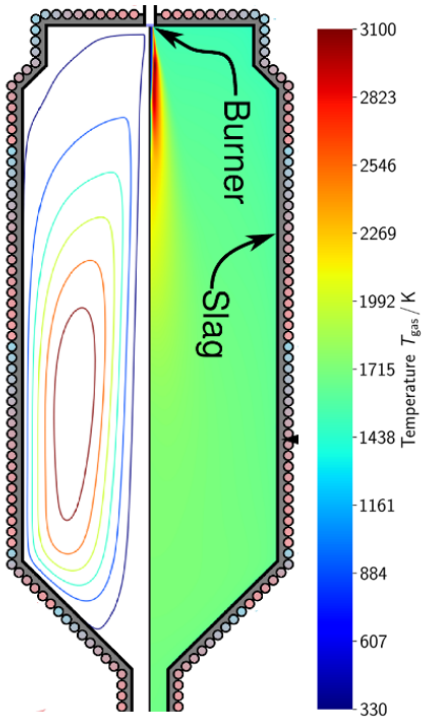


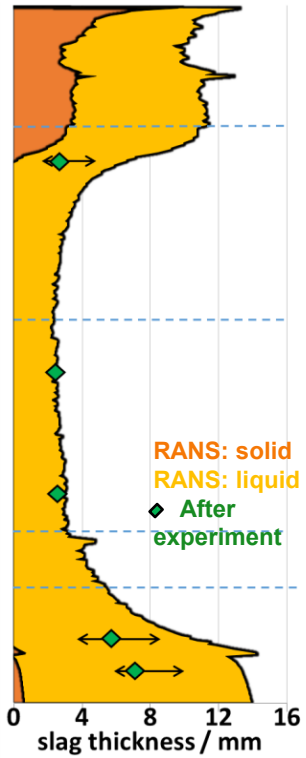
# bioliq® - EFG, modeling/balancing

## slagging and heat release




Glycol + wood char ; 5 MW ; 40 bar ; $\lambda_{tech}$ = 0,56 ; $T_{ad}$ = 2381 K

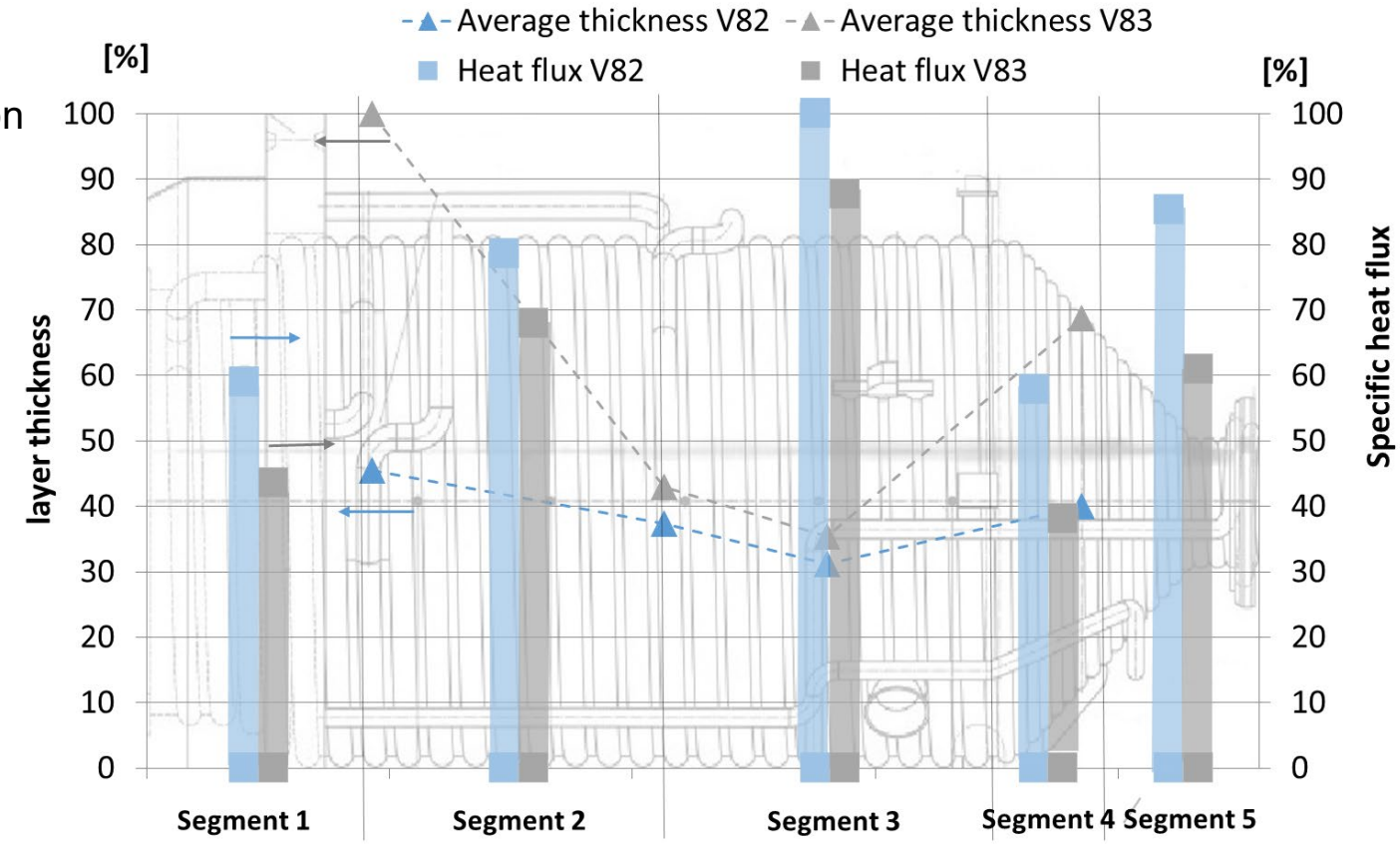
Seebold et al., *Thermophysical and chemical properties of bioliq slags*, Fuel, Vol.197, June 2017, Pages 596-604

# bioliq® - EFG, experimental

## slag layer thickness and heat flux

V82 ➔ V83
Reduction of gasification temperature by 55 K

Slag layer on cooling screen

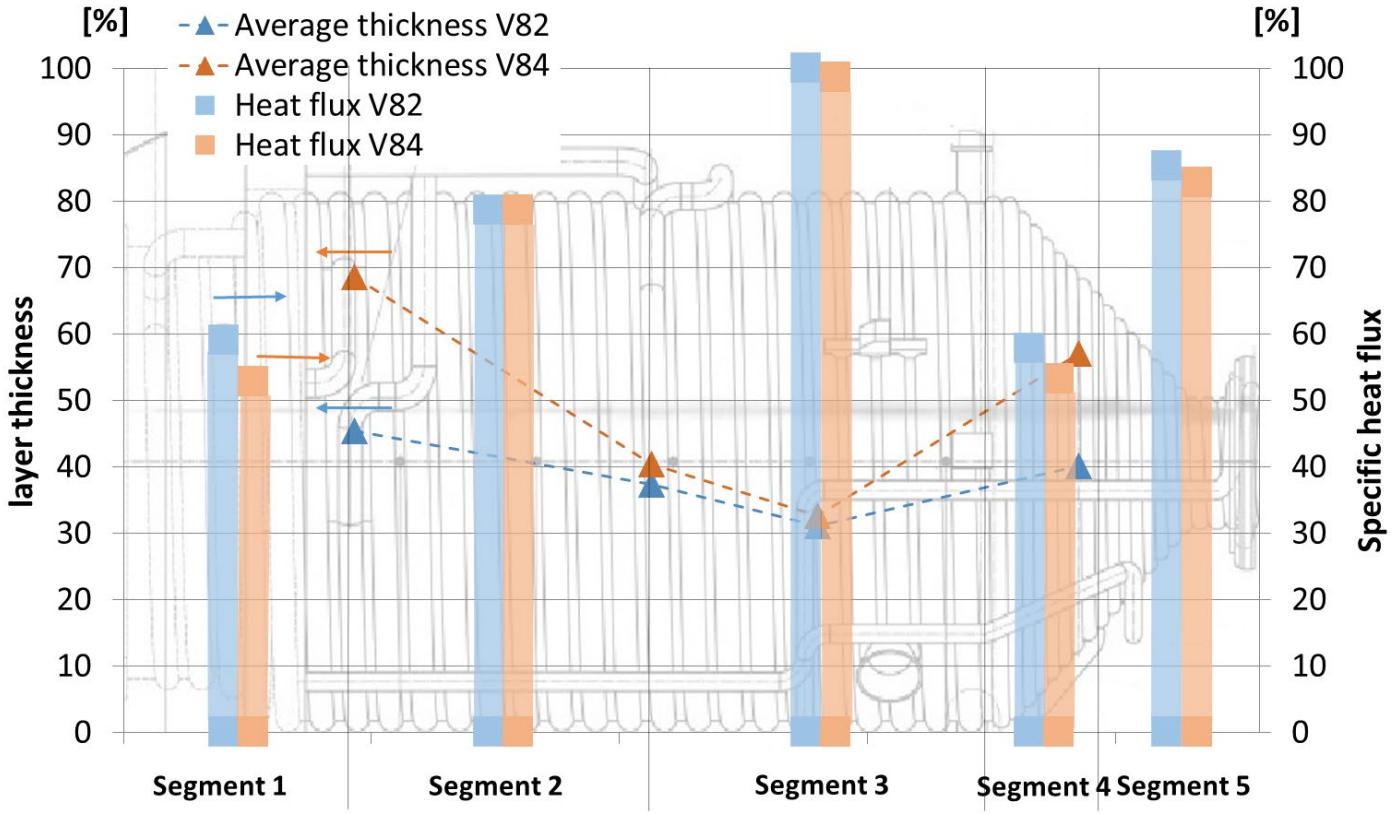


# bioliq® - EFG, experimental

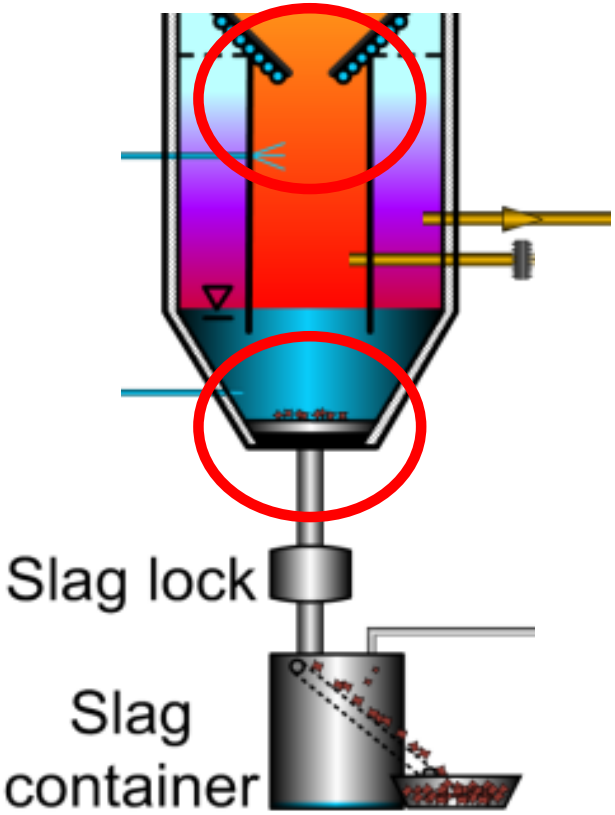
## slag layer thickness and heat flux

V82 ➔ V84
Doubling the amount of ash components

Slag layer on cooling screen



# bioliq® - EFG, optimization slag discharge




## Challenge:

Frequently clogging at quench cone

*Caused by slag lumps*

## Solution:

*Adjust slag viscosity and flow temperature by:*

- reactor temperature
- additives

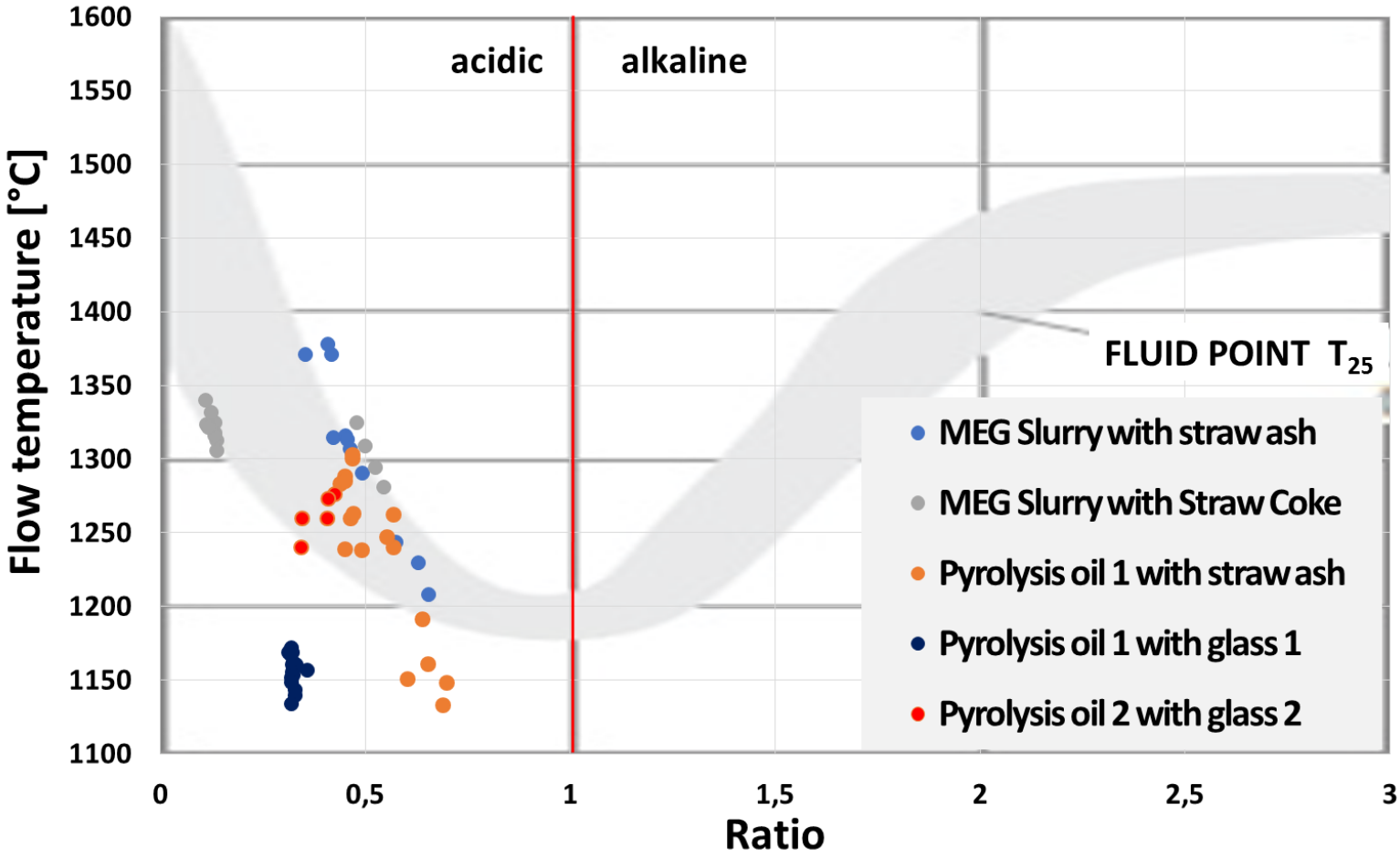
*Adjust thermal conditions at reactor outlet by:*

- slag amount
- quench cooling

*Integration of a slag crusher*

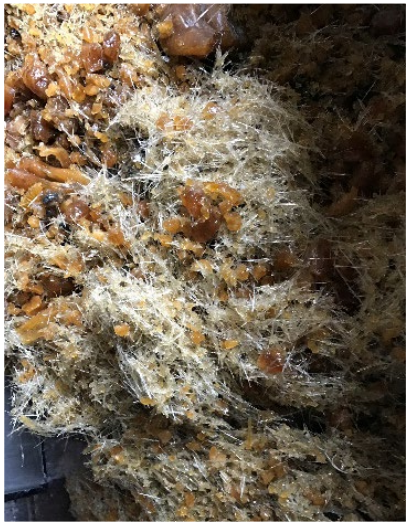
# bioliq® - EFG, optimization slag discharge

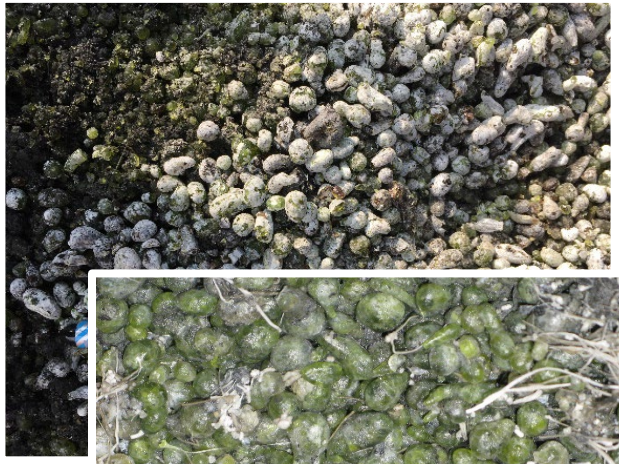
## slag flow temperature vs. acidic-alkaline ratio

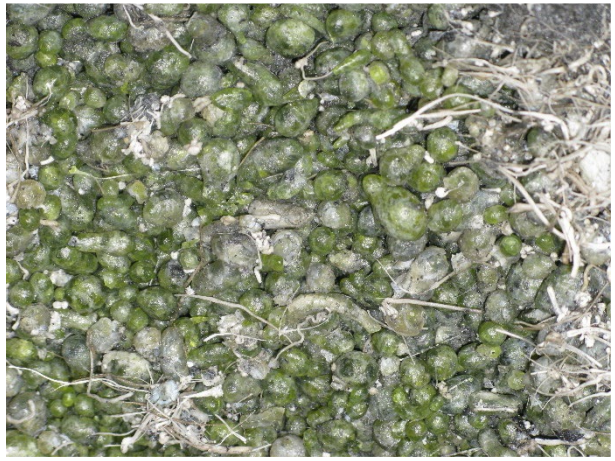



$$\text{RATIO R} = \frac{CaO + MgO + Fe_2O_3 + Na_2O + K_2O}{SiO_2 + Al_2O_3 + TiO_2}$$

# bioliq® - EFG, slag structures



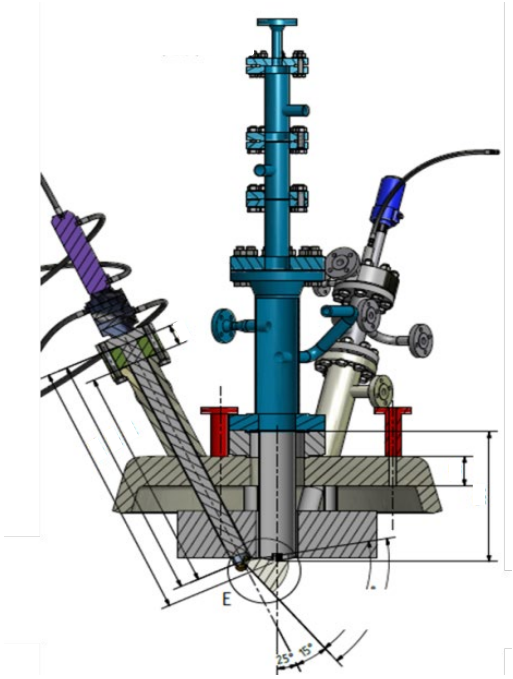


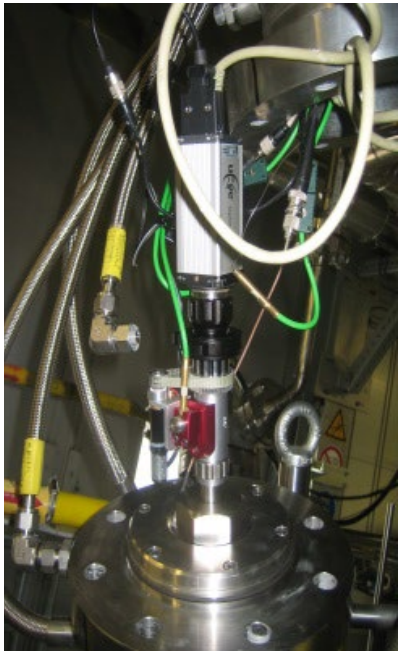


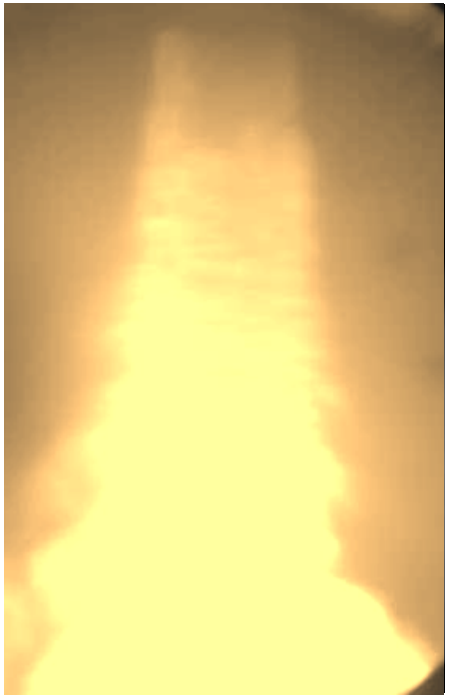
# bioliq® - EFG, development of diagnostic tools

**Example: High Pressure Optical Borescope**
camera based systems for analysis of atomization

- High Dynamic Range Camera
- High Speed Camera







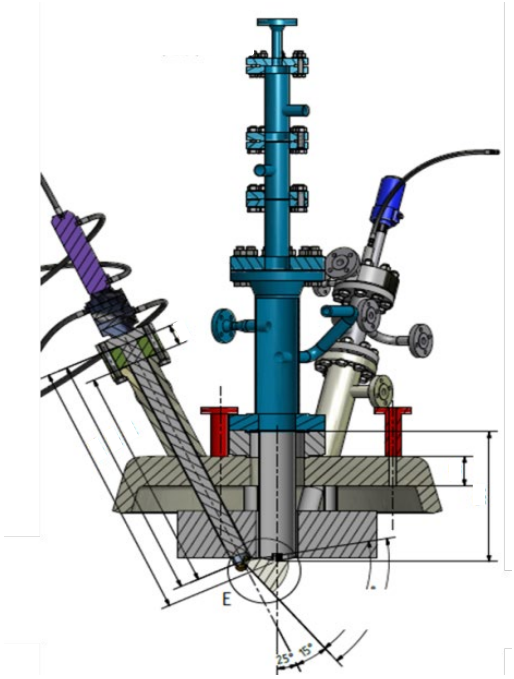
Gasifier flame at 40 bar

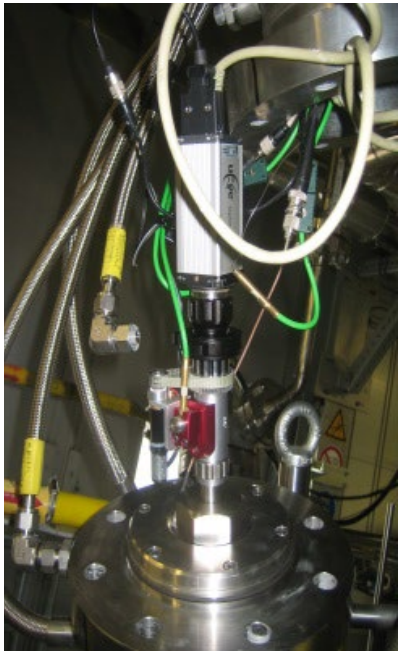
Cooperation with KIT Institute for Applied Computer Science, IAI

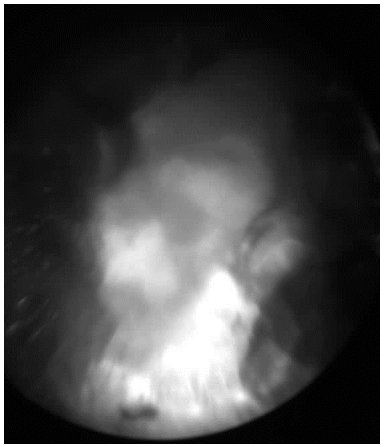
# bioliq® - EFG, development of diagnostic tools

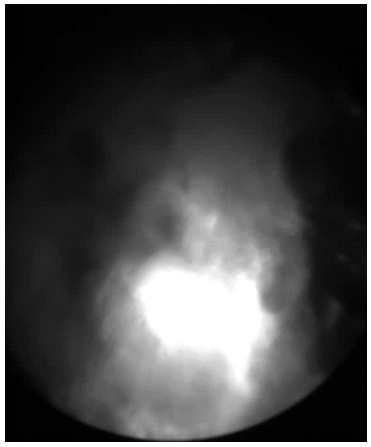
**Example: High Pressure Optical Borescope**
camera based systems for analysis of atomization

- High Dynamic Range Camera
- High Speed Camera









**Increase in the**
**recording rate 50 fps → 3500 fps (slow motion)**
Exposure time 30µs

Cooperation with KIT Institute for Applied Computer Science, IAI

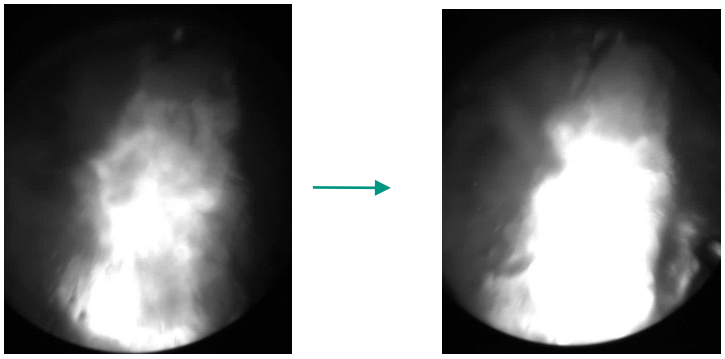
# bioliq® - EFG, development of diagnostic tools

## Example: High Pressure Optical Borescope
camera based systems for analysis of atomization

**Glycol + 4,5% A-Glass**

| Versuchsnr. | λ | Brennstoff-leistung | Brennstoff-menge | Zerstäuber-dampfmenge | ZD / BS | Dampf zu Sauerstoff |
|---|---|---|---|---|---|---|
| V107.1 Grundeinstellung | 0,45 | 4,5 MW | 990 kg/h | 199 kg/h | 0,2 | 73,5 kg/h |
| V107.2 | 0,45 | 4,5 MW | 990 kg/h | 100 kg/h | 0,1 | 67,9 kg/h |
| V107.3 | 0,55 | 4,5 MW | 990 kg/h | 199 kg/h | 0,2 | 62,2 kg/h |
| V107.4 | 0,55 | 3,5 MW | 768 kg/h | 155 kg/h | 0,2 | ~52 kg/h |
| V107.5 Grundeinstellung | 0,45 | 4,5 MW | 990 kg/h | 199 kg/h | 0,2 | 73,5 kg/h |

V107.**1** V107.**2**



**Reduction of atomization steam about 50%**

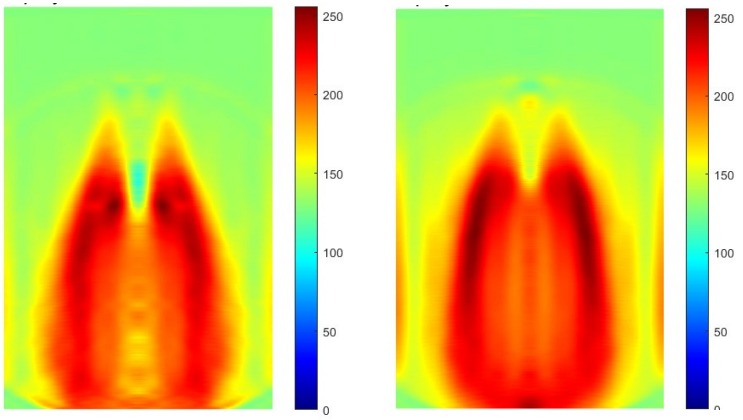
**200 kg/h → 100 kg/h**

Exposure time 30µs, Real Time 50 fps

Abeln Inversion → Averaging of light intensity over 1000 images, mirroring of the mean value images at the center axis.

Abel Inversion V107.**1** (30µs) 3500fps

Abel Inversion V107.**2** (30µs) 3500fps




Reduction of the atomizing medium leads to higher radiation intensity

Cooperation with KIT Institute for Applied Computer Science, IAI

# bioliq® - EFG, development of diagnostic tools

## Example: High Pressure Optical Borescope
camera based systems for analysis of atomization

**Glycol + 4,5% A-Glass**

| Versuchsnr. | λ | Brennstoff-leistung | Brennstoff-menge | Zerstäuber-dampfmenge | ZD / BS | Dampf zu Sauerstoff |
|---|---|---|---|---|---|---|
| V107.1 Grundeinstellung | 0,45 | 4,5 MW | 990 kg/h | 199 kg/h | 0,2 | 73,5 kg/h |
| V107.2 | 0,45 | 4,5 MW | 990 kg/h | 100 kg/h | 0,1 | 67,9 kg/h |
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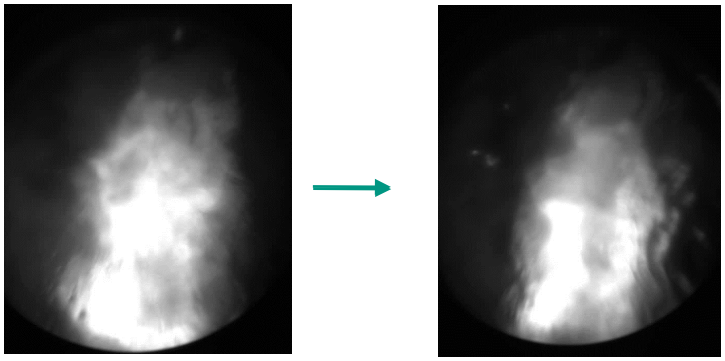
| V107.4 | 0,55 | 3,5 MW | 768 kg/h | 155 kg/h | 0,2 | ~52 kg/h |
| V107.5 Grundeinstellung | 0,45 | 4,5 MW | 990 kg/h | 199 kg/h | 0,2 | 73,5 kg/h |

V107.**1** V107.**3**



**Increase of Lambda: 0,45 → 0,55**

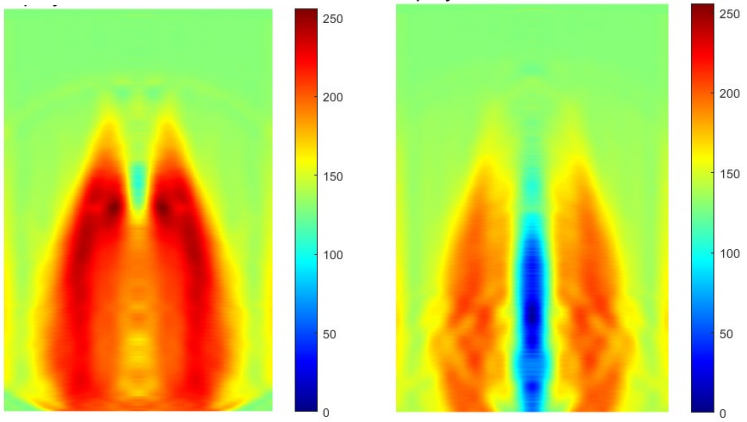
Exposure time 30µs

Real Time 50 fps

Abeln Inversion → Averaging of light intensity over 1000 images, mirroring of the mean value images at the center axis.

Abel Inversion V107.**1** (30µs) 3500fps

Abel Inversion V107.**3** (30µs) 3500fps

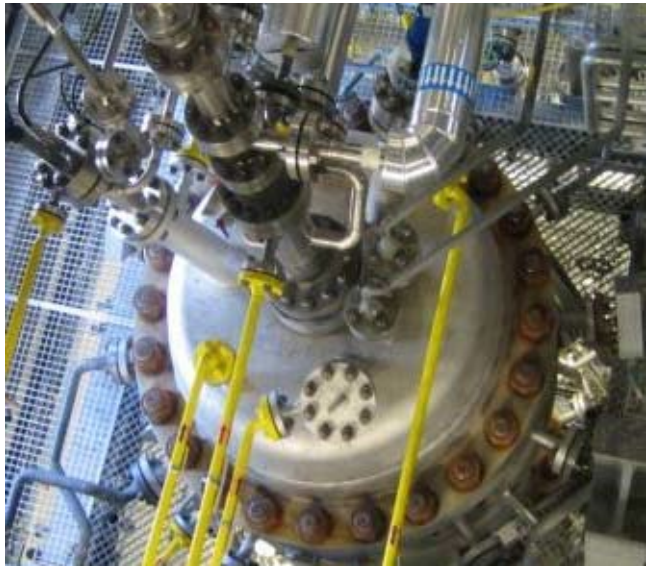



Increase of Lambda leads to lower radiation intensity

Cooperation with KIT Institute for Applied Computer Science, IAI

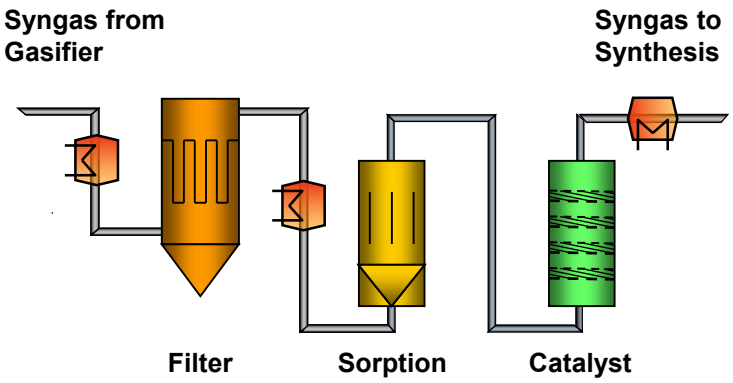
# bioliq® - EFG, status quo

- Since 2013 about 1690 tons of different slurries processed at approximately 2250 hours of operation with different slurries
- Slurry compositions
  - Organic condensate of bioliq® fast pyrolysis
  - Wood based pyrolysis oils
  - Ethylene glycol as model fuel
  - With different types of solids (wood- / straw char, ashes, glass)
- Ongoing optimization in
  - Fuel flexibility
  - Slagging behavior
  - Online-diagnostics



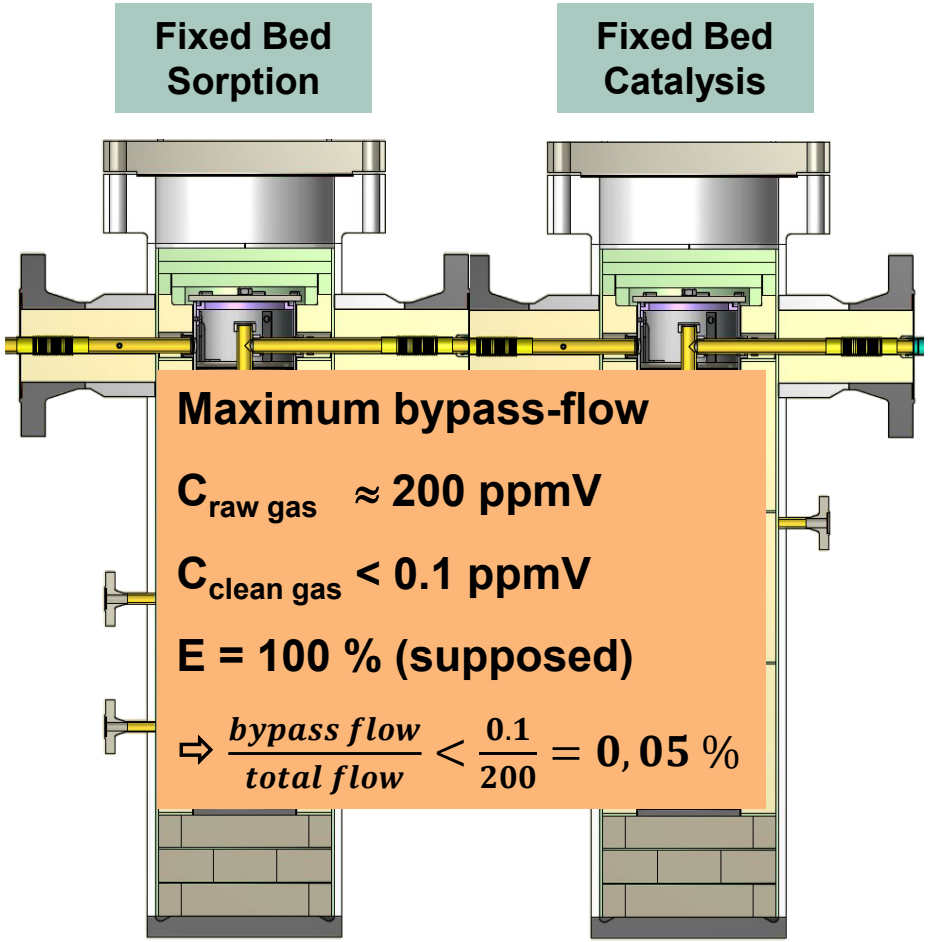
# bioliq® - hot gas cleaning

- Main features HTHP gas cleaning
  - Operation up to 80 bar and up to 800 °C
  - Load range 700 Nm³/h Syngas (2 $MW_{th}$)
  - Ceramic filter candles, mounted horizontally
  - Re-cleaned by Couple-Pressure-Pulse (CPP)
  - Fixed bed sorption for sour gases, alkali and heavy metals
  - Catalyst bed for N-species and hydrocarbons decomposition




- Challenges
  - Meet extremely low target levels of contaminants (< 0.1 mg/m³ STP) for catalytic syngas conversion
  - Long term operation behavior

# bioliq®- hot gas cleaning, reactor design




## Functional Separation of High-Temperature and High-Pressure

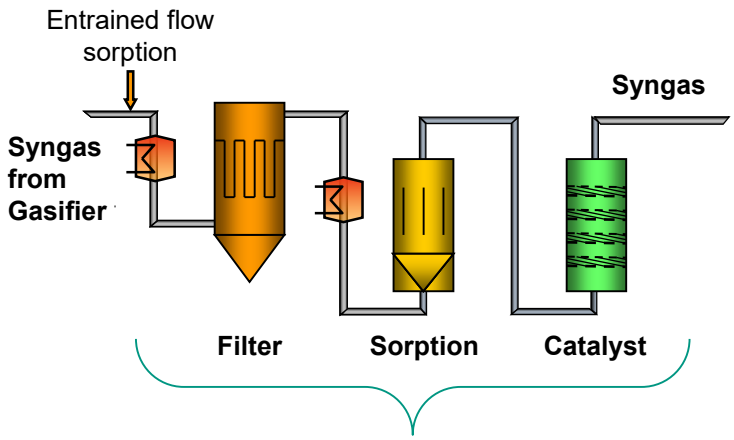
- Syngas-tubes (inside)
  *max. temperature* *800 °C*
  *low overpressure* *0.5 bar*
- Pressure Vessel (outside)
  *max. temperature* *350 °C*
  *max. overpressure* *85 bar*

## Challenge

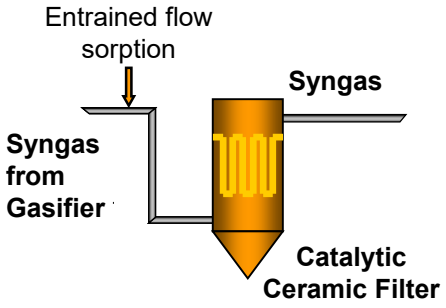
- Connections of syngas-tubes are not absolutely gas tight
- Avoidance of syngas-bypass-flow through insulation

# bioliq® - hot gas cleaning, status quo

- Required purity specifications for sour gases achieved with fixed bed adsorption at 700 °C / 400 °C
- Online-gas-analysis for S, Cl and N species proofed (clean and raw gas side)

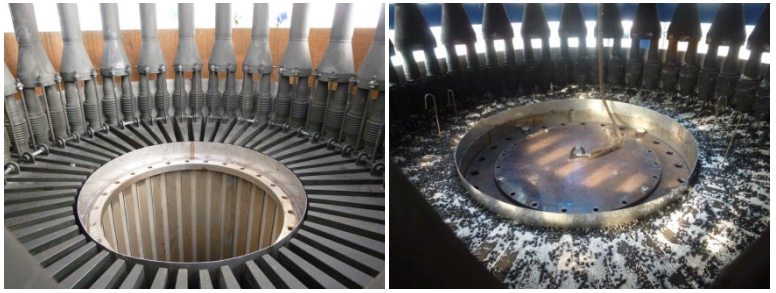



- Ongoing work
  - Investigation of different HTHP-sorbents mixtures with improved measurement technology
  - Construction and commissioning of a dry entrained flow adsorption for continuous operation

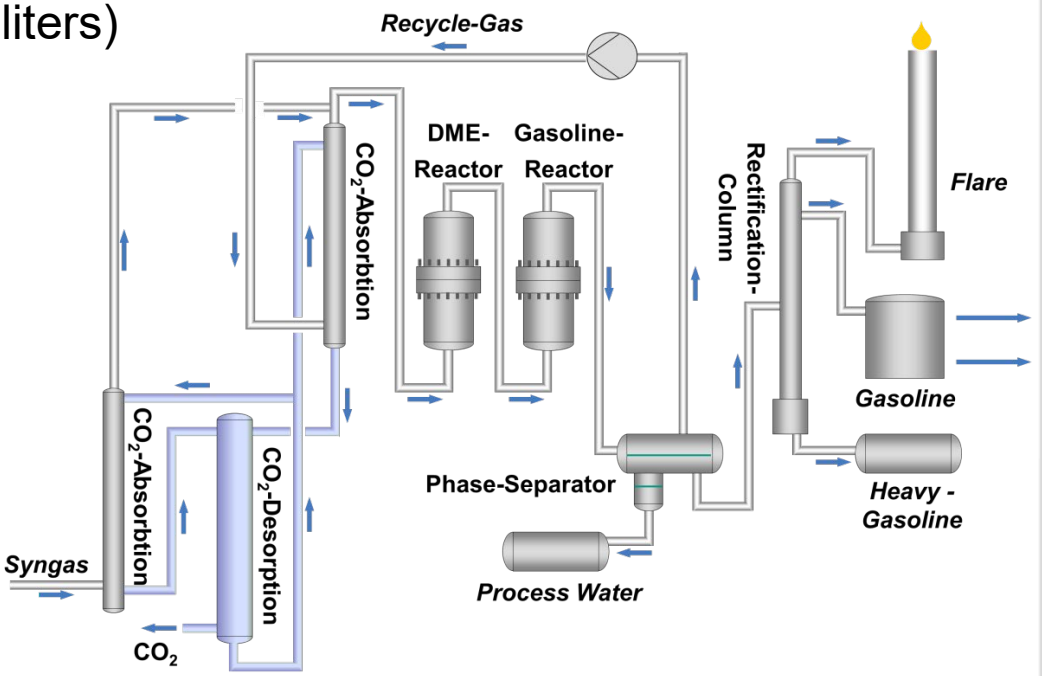


# bioliq® - fuel synthesis

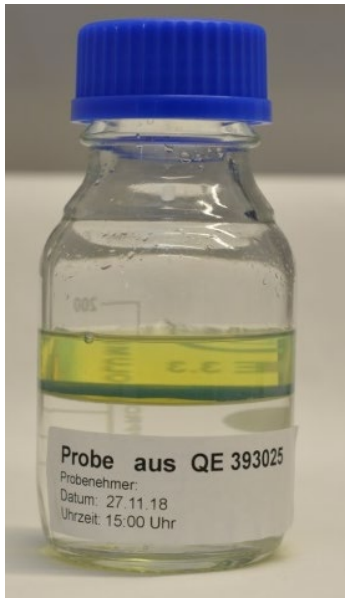
- Main features
  - Operation up to 60 bar
  - Load range 700 Nm³/h Syngas (2 $MW_{th}$)
  - One step DME synthesis, operated at 240 - 250 °C ($V_{catalyst}$ = 1000 liters)
  - Gasoline synthesis, operated at 350 - 370 °C ($V_{catalyst}$ = 600 liters)



Empty and filled reactor/heat-panel beds

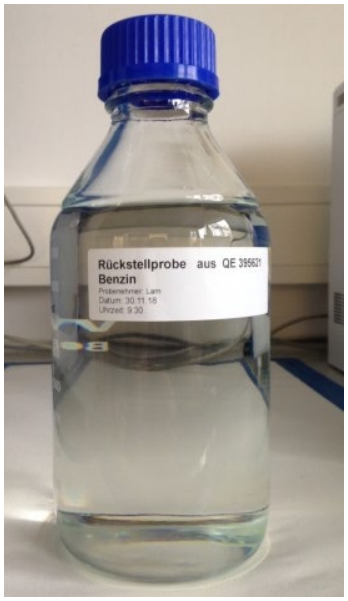


# bioliq® - fuel synthesis, product




Raw Gasoline


Raw Gasoline-Mix




Rectification top-product


Rectification bottom-product

# bioliq® - fuel synthesis, status quo

- Revision of both reactors in 2017 for improved temperature and residence time behavior
  ⇒ CO conversion increased by a factor of 2.5
- Production of 5200 l bio-based raw gasoline in 830 h (8 campaigns) since Nov / Dec 2017
- Syngas bottling (200 bar) for external applications

AMBITION

- Application tests of different fuel blends: reFuels project in Baden-Württemberg state with automotive industry, oil refinery

*Syngas bottling*

KIT Karlsruher Institut für Technologie coordination

C·A·C® Chemieanlagenbau Chemnitz GmbH

# bioliq® pilot plant - next steps

- After proof of concept has been achieved in 2017, work is focused on efficiency improvement and further development of process components
- Continued R&D activities within HGF-research program, national and international projects (20 Phd works ongoing):
  - Feedstock flexibility and process efficiency
  - Scalability from lab- to pilot- to commercial scale
- Development of concepts for process implementation, including $CO_2$ utilization by external hydrogen production
- Back bone of EnergyLab 2.0 at KIT for Energy Transition in Germany

# Thanks to…

- funding agencies and institutions
- partners from industry and academia
- the teams from KIT
- …and to the audience

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