Karlsruher Institut für Technologie

Hot gas cleaning – Experiences and improvements at the bioliq pilot plant

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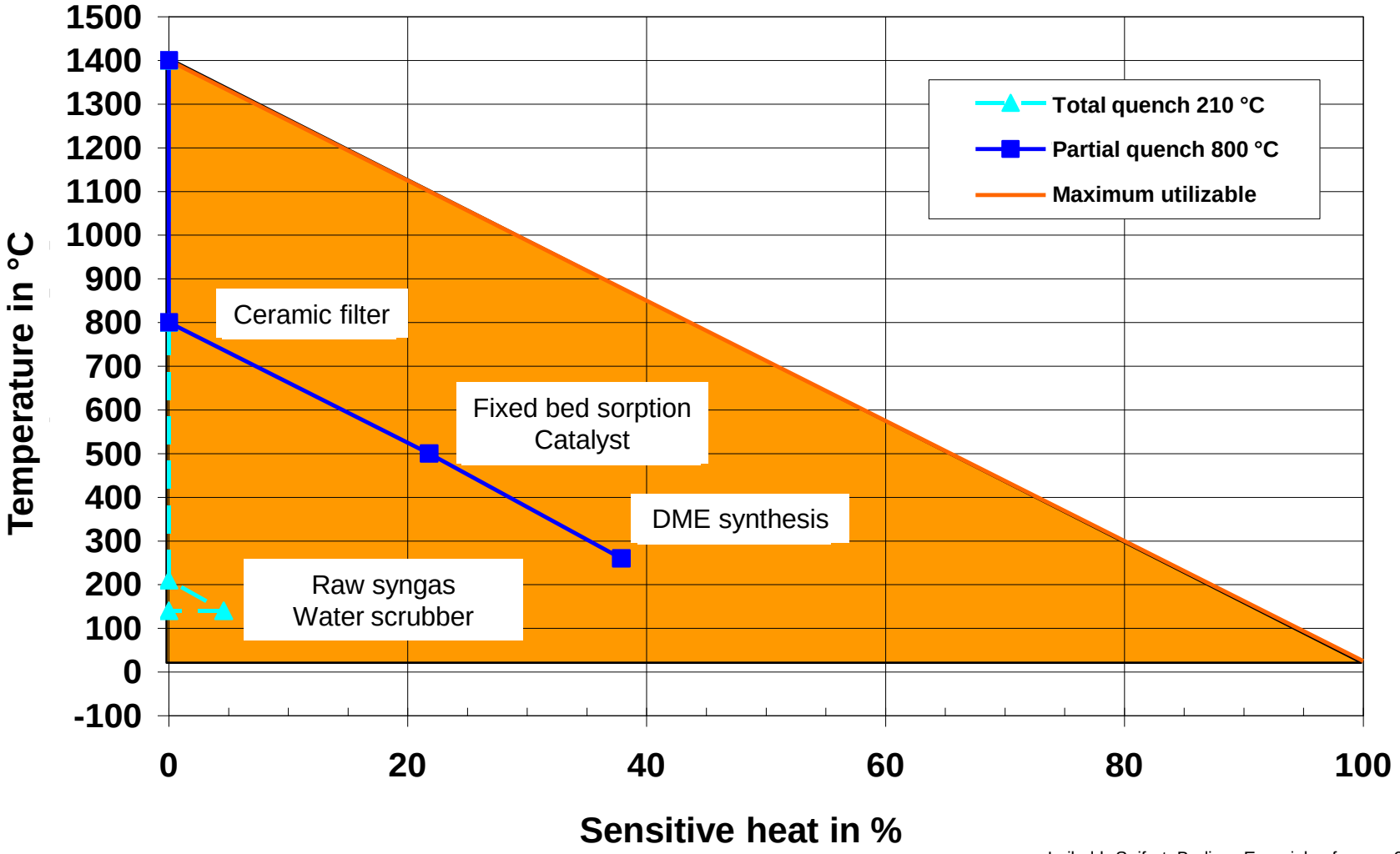
Process efficiency – heat recovery

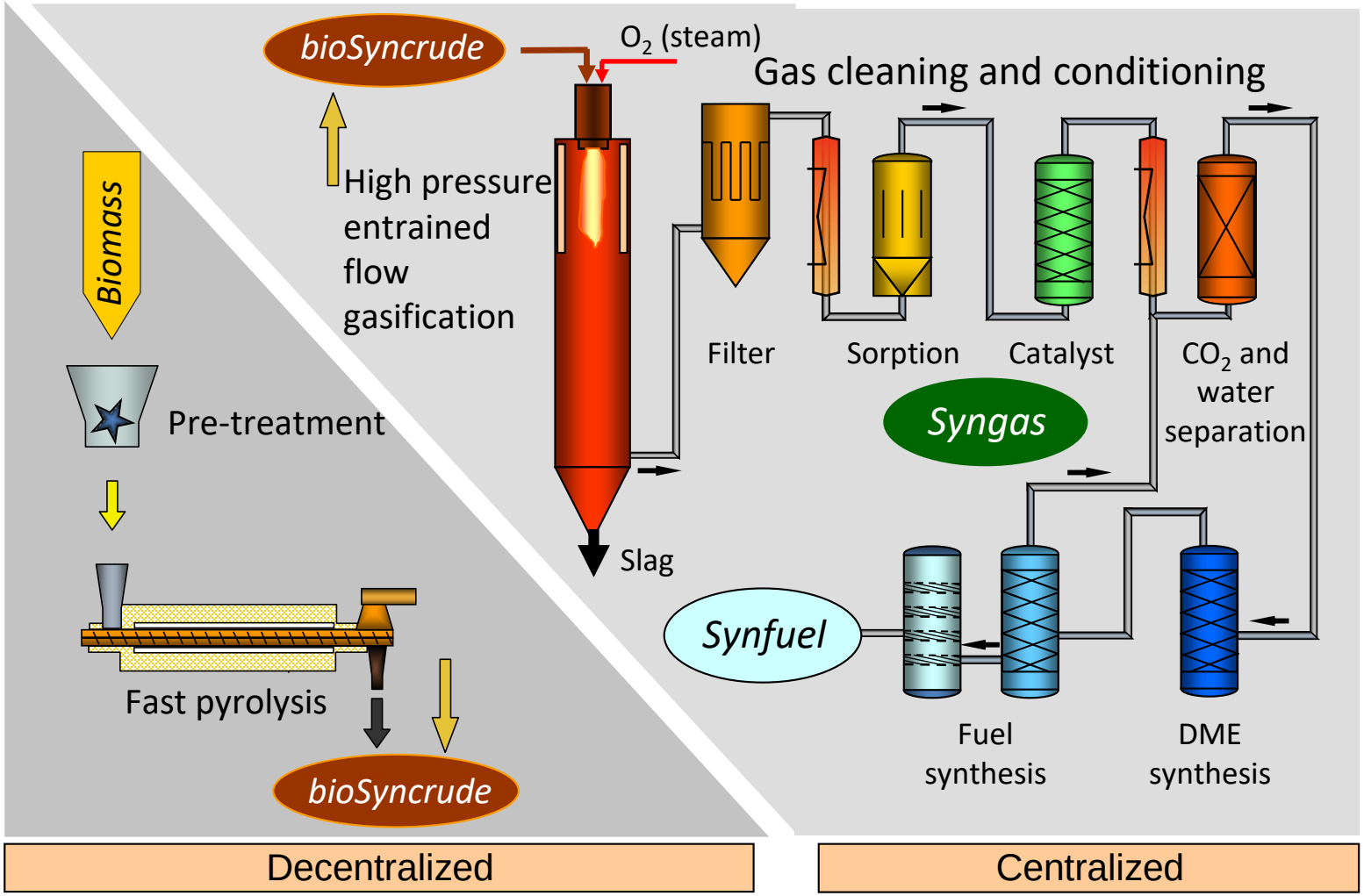


Leibold, Seifert, Berliner Energiekonferenz, 2010

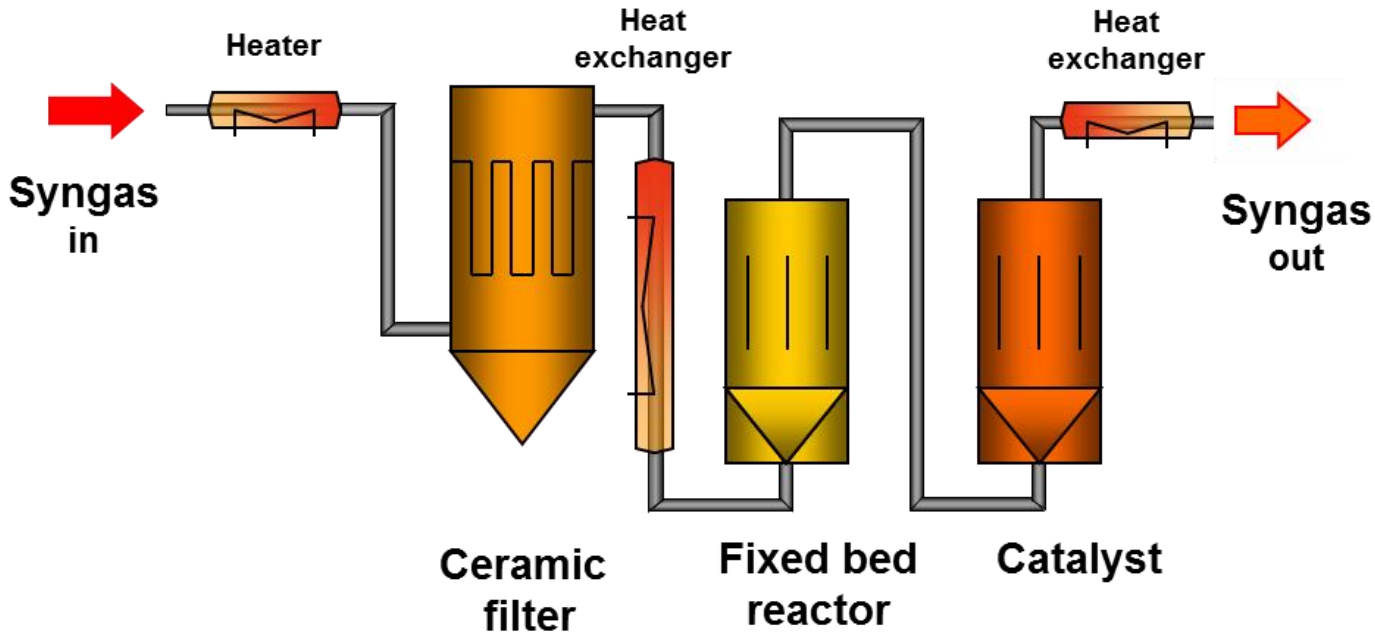
Contaminants in biogenic syngas & Clean gas specifications of utilization technologies

mg/Nm³	Gasification	Gas motor[1]	Gas turbine	SNG	MeOH[1]	FT[2]
Particulates	10^4 - 10^5	< 50	< 1	< 0,5	0.2	n.s.
Tar	0 - (20 000)	< 100	< 5	< 0,1	< 1	n.s.
Na + K	0.5 - 5	n.s.	< 0.2	< 1	< 0.2	< 0.01
NH_3 + HCN	200 - 2000	< 55	n.s.	< 0,8	< 0.1	< 0.02
H_2S + COS + CS_2	50 - 100	< 1150	< 1	< 0,4	< 0.1	< 0.01
Halogenes	0 - 300	n.s.	< 1	< 0,06	< 0.1	< 0.01
Heavy metals	0.005 - 10	n.s.	n.s.	n.s.	n.s.	< 0.001

The bioliq® process



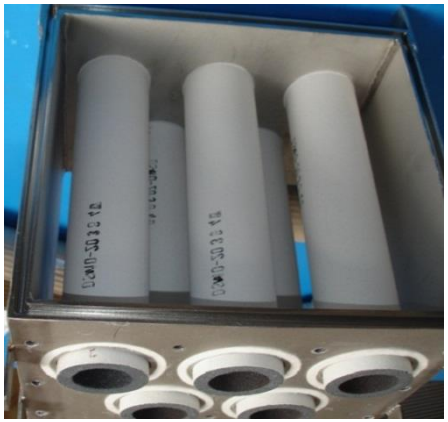
Dry HTHP cleaning bioliq



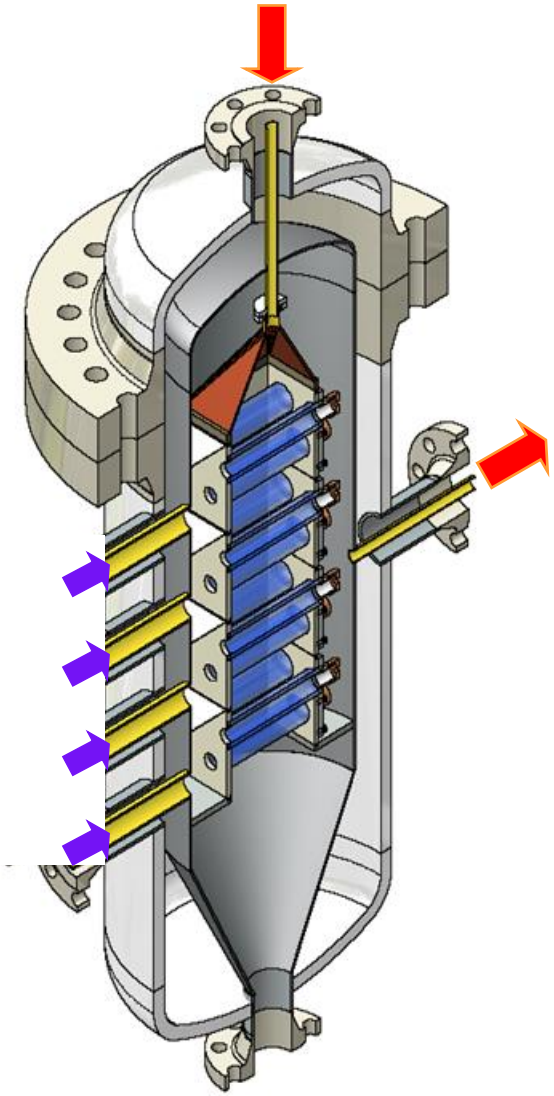
- Syngas flow: 700 m³/h STP @ 800 °C / 80 bar
- Particulate filtration ➔ ceramic elements; CPP recleaning
- Fixed bed sorption ➔ HCl, H_2S, COS, alkali
- Catalyst bed ➔ Organics, NH_3, HCN

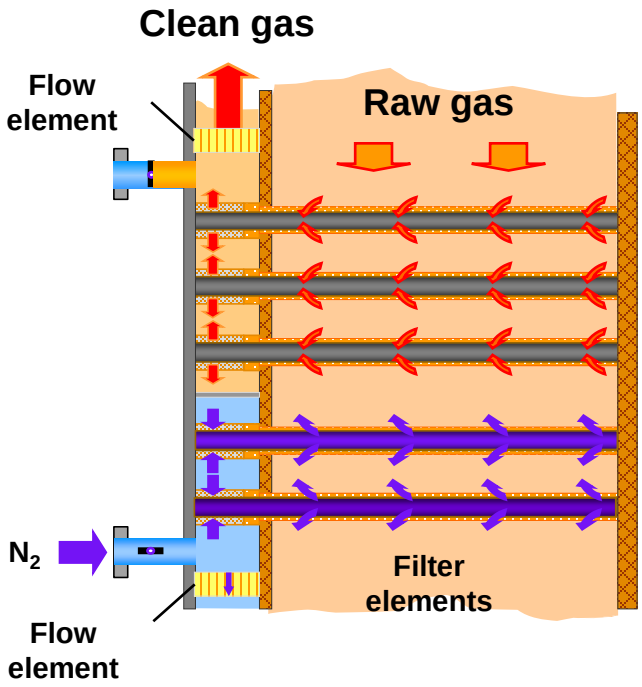
HTHP horizontal filter system bioliq®

Filter element (detail)



Filter section





Dry HTHP sorption of trace contaminants HCl, H_2S

- Cost effective alkali/earthalkali carbonates
- Low level equilibria concentrations in syngas
- Solid reaction products
- Sorption kinetics enable serial sorption process of chlorides and sulfides
- Temperature and pressure influence on sorption process

$$NaHCO_3,\ Na_2CO_3 \cdot 2\,H_2O + HCl + H_2S = 2\,CO_2 + 4\,H_2O + NaCl + Na_2S$$

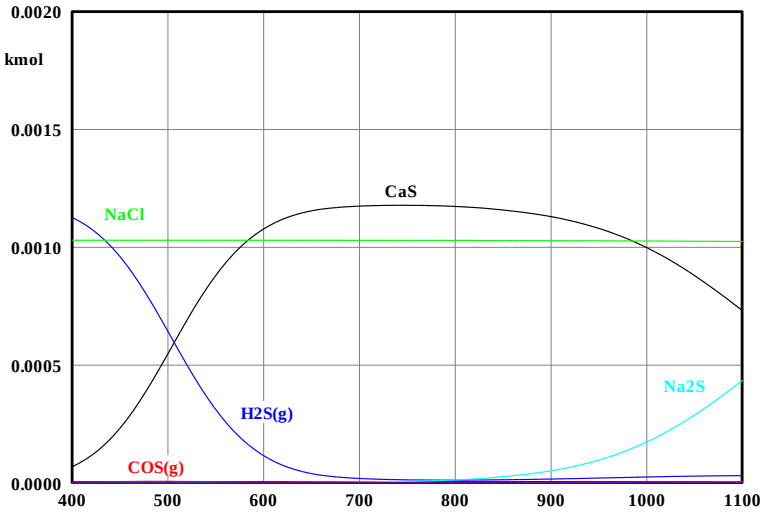
$$Na_2CO_3 + H_2O = 2\,NaOH + CO_2$$

$$3\,NaOH + HCl + H_2S = NaCl + Na_2S + 3\,H_2O$$

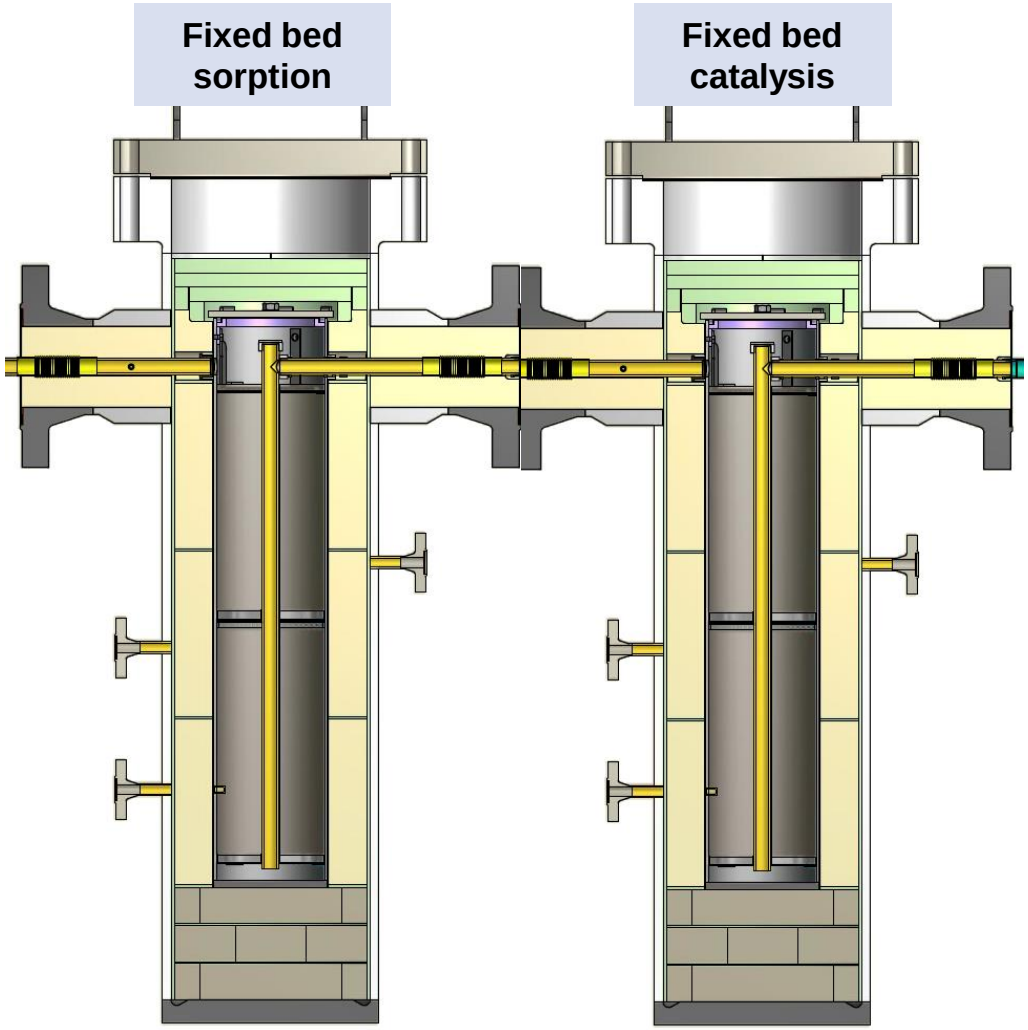
$$2\,CaCO_3 + 2\,HCl + H_2S = 2\,CO_2 + 2\,H_2O + CaCl_2 + CaS$$

$$CaCO_3 = CaO + CO_2$$

$$2\,CaO + 2\,HCl + H_2S = CaCl_2 + CaS + 2\,H_2O$$



Sorption / catalyst reactors

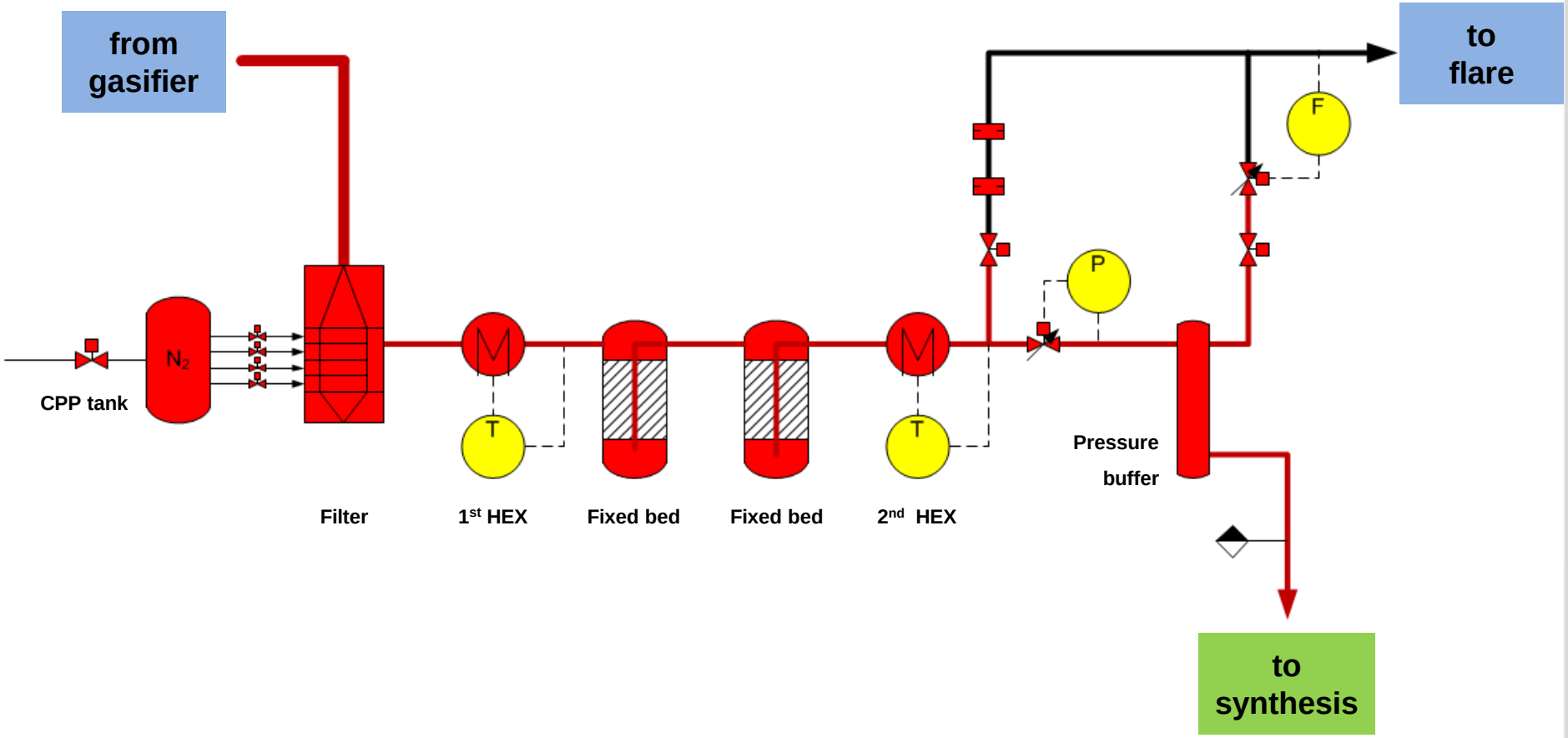


- Functional separation of HT and HP challenge
  - Pressure vessels
    max. temperature 350 °C
    max. overpressure 85 bar
  - Syngas contacting vessels/tubes
    max. temperature 800 °C
    low overpressure 0.5 bar
- 2 staged design for sorption and catalyst reactor
  - Top-down flow inside reactors
  - Residence time 1 sec per stage
  - Pelletized sorbents and catalysts
- N_2 sealing gas concept enables removable joints
- Total life time limited to ~ 100 h

Variabilty in design of HTHP cleaning units

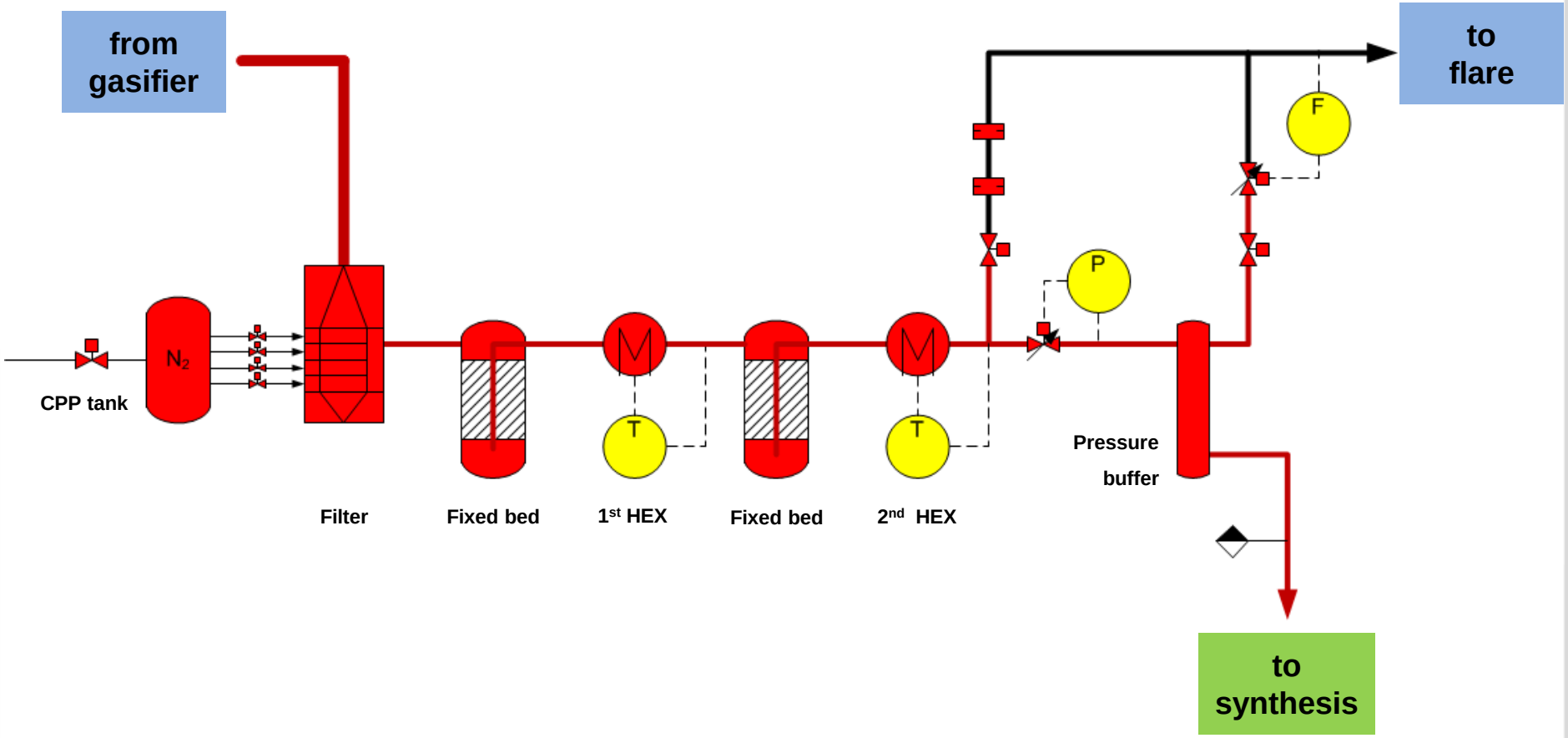
Flexibility of bioliq® HTHP syngas cleaning

Initial design



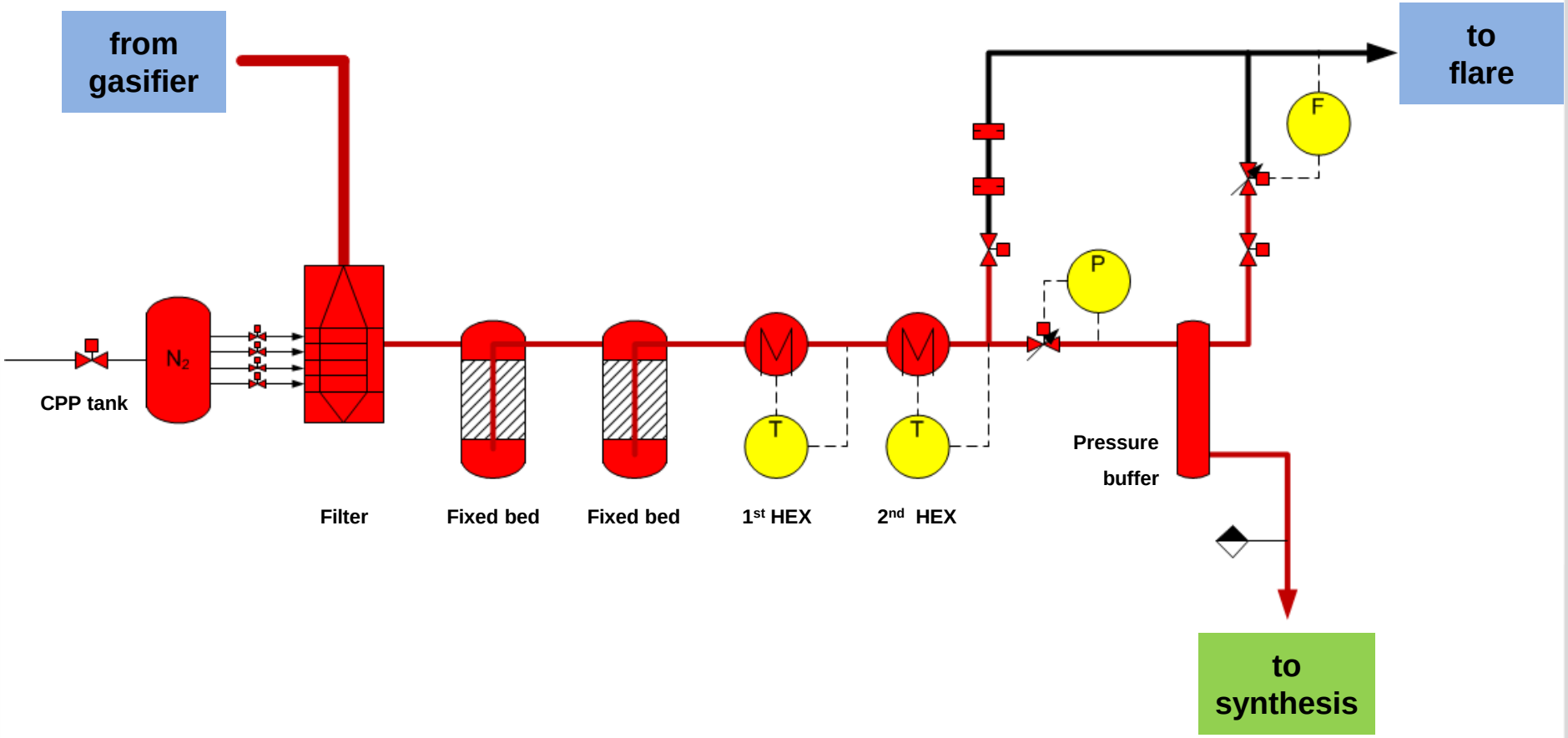
Flexibility of bioliq® HTHP syngas cleaning

Staged temperature sorption and catalysis



Flexibility of bioliq® HTHP syngas cleaning

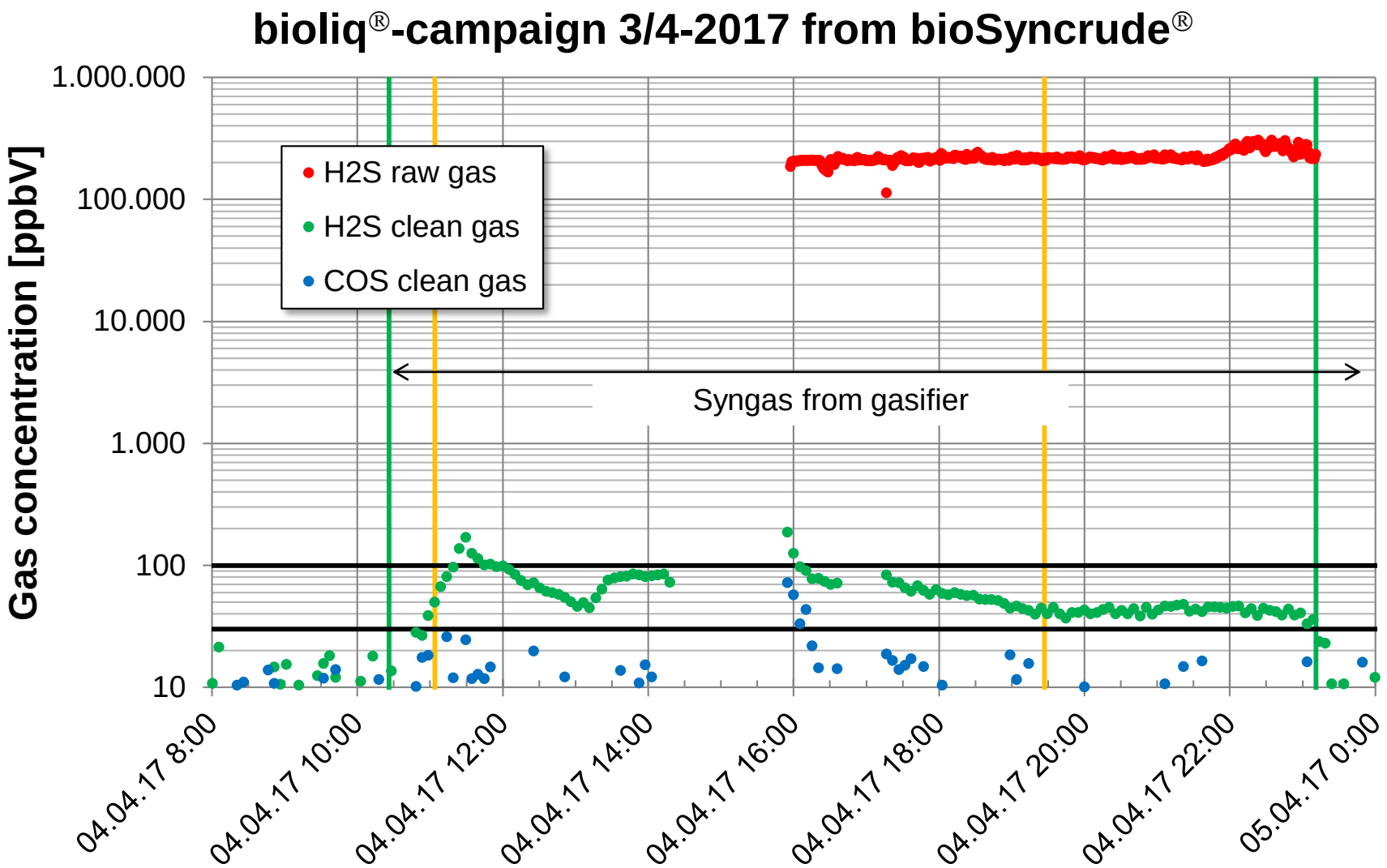
Uniform temperature sorption and catalysis



bioliq campaigns 2017-2019 HTHP gas cleaning

	3/4-2017	11/12-2017	3/4-2018	11/12-2018	5-2019
Feed	Wood/bioSyncrude	Wood	Wood	bioSyncrude	Wood
Syngas mass flow	250 kg/h	250 kg/h	250 kg/h	250 kg/h	350 kg/h
Ceramic filter	600-650 °C	750 °C	650-750 °C	650 °C	650 °C
Sorption	350-450 °C	400-500 °C	400-500 °C	350-400 °C	350-450 °C
Catalyst	-	CuO/Cr_2O_3	-	-	-
H_2S	30-110 ppb	30-150 ppb	30-70 ppb		
COS	<< 20 ppb	30-150 ppb	<< 10 ppb	<< 10 ppb	<< 10 ppb
HCl	<10 ppb	(1-1.5 ppm)			
NH_3	60-150 ppm				60-75 ppm
HCN	0.13-0.25 ppm				

Results H_2S and COS

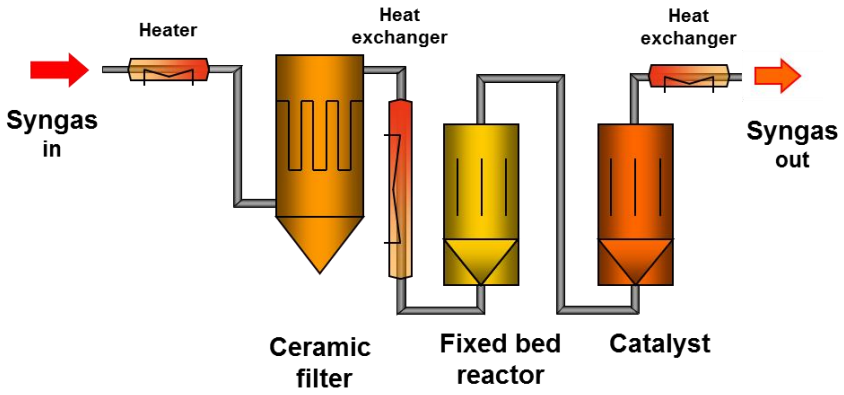


Integrated hot gas treatment concept bioliq

✓ Process chain HTHP syngas cleaning

- Filtration of sticky and reacting particles
- Dry fixed bed sorption of trace contaminants HCl, H_2S, COS, alkali species
- Catalytic decomposition of NH_3, HCN, trace organics

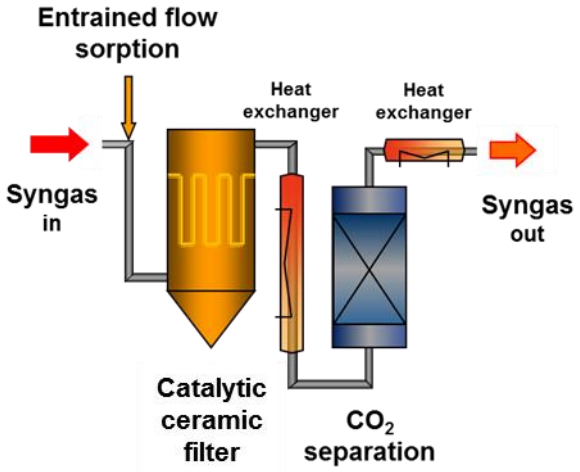
bioliq HTHP syngas cleaning 2019



➢ Integrated syngas treatment

- Scalability and long-term performance
- Design and implementation of entrained flow sorption process
- Development of catalytically coated ceramic fiber filter
- Implementation of HTHP CO_2 separation process

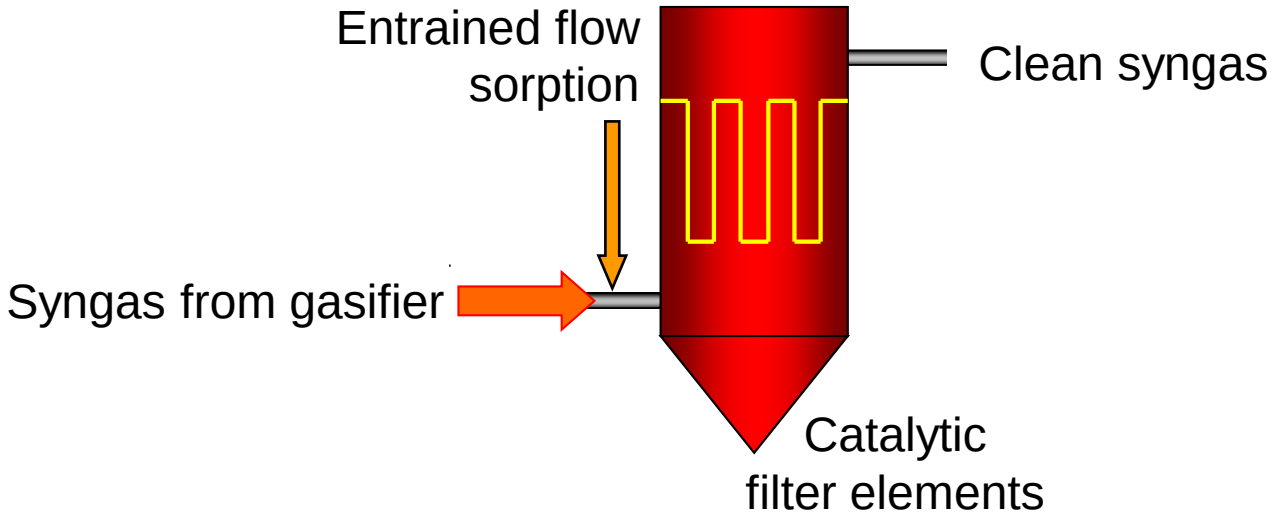
bioliq HTHP integrated syngas treatment



Why entrained flow sorption process

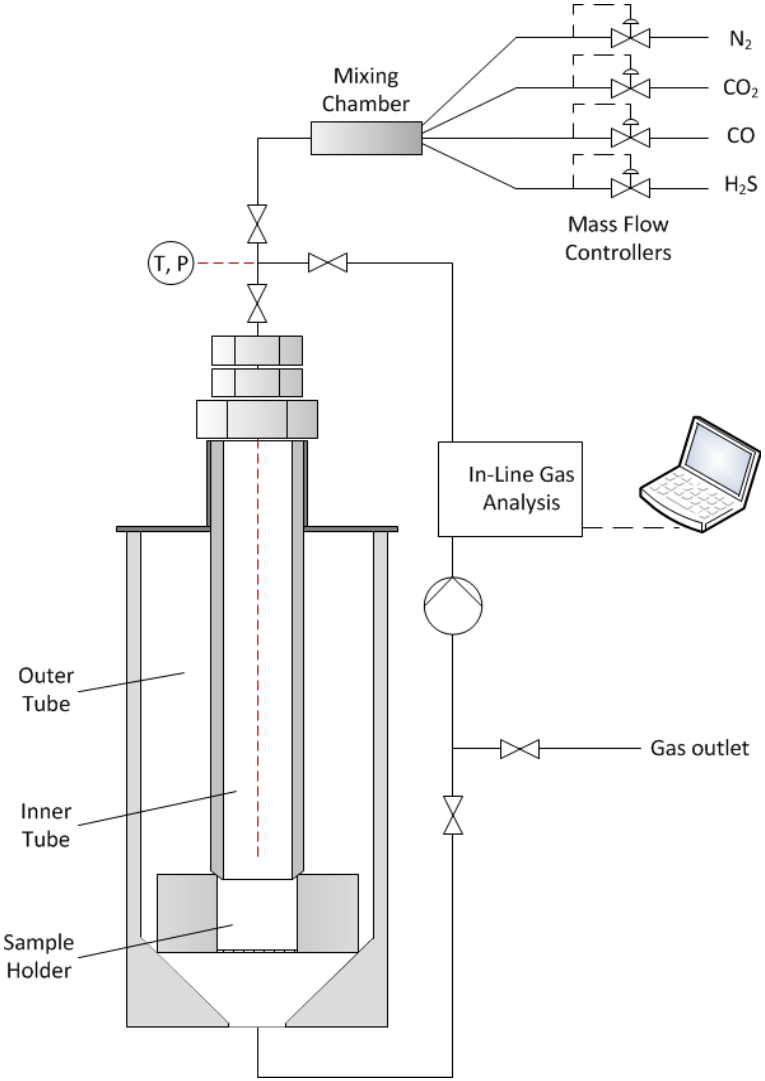
- Enable continuous sorption process for trace contaminants
- Adapt to variable contaminants` concentrations
- Utilize pulverized sorbents to enhance sorption process
- Sorption properties instead of thermo-mechanical properties
- Exclude channelling and bypassing
- Utilize liquid sorbents dispersions
- Enable further process integration

Entrained flow sorption process



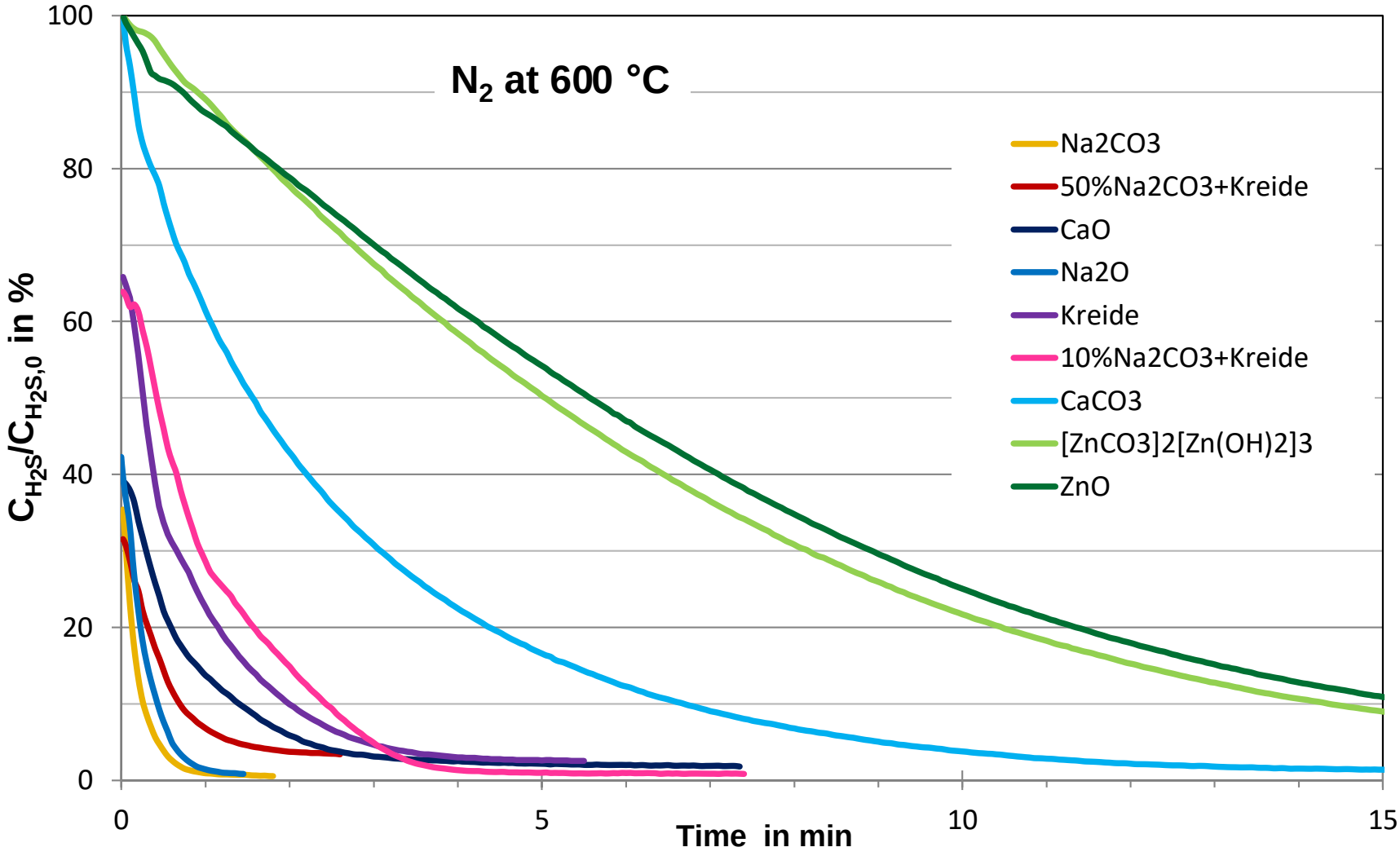
- Sorption material/sorbents mixture?
- Sorption kinetics?
- Sorption process?

Kinetics measurement device

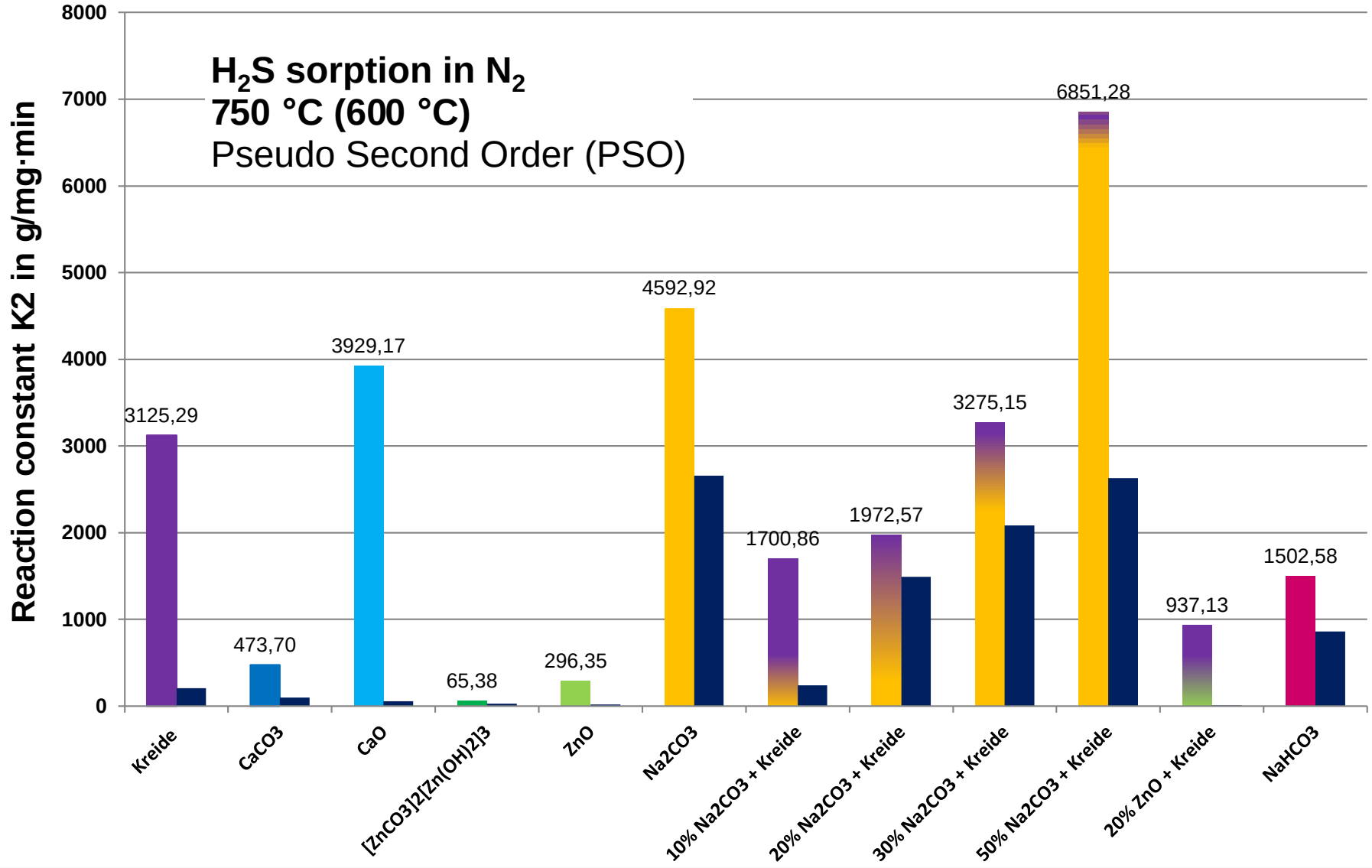


Temperatures:	up to 800°C
Reaktor volume:	$3{,}5 \cdot 10^{-5}$ m^3
Sample:	100 mg
t_R :	0,01 – 0,006 s
Gas flow:	0,03 – 0,12 m^3/h

H_2S sorption kinetics – experimental results



H_2S sorption kinetics - temperature influence

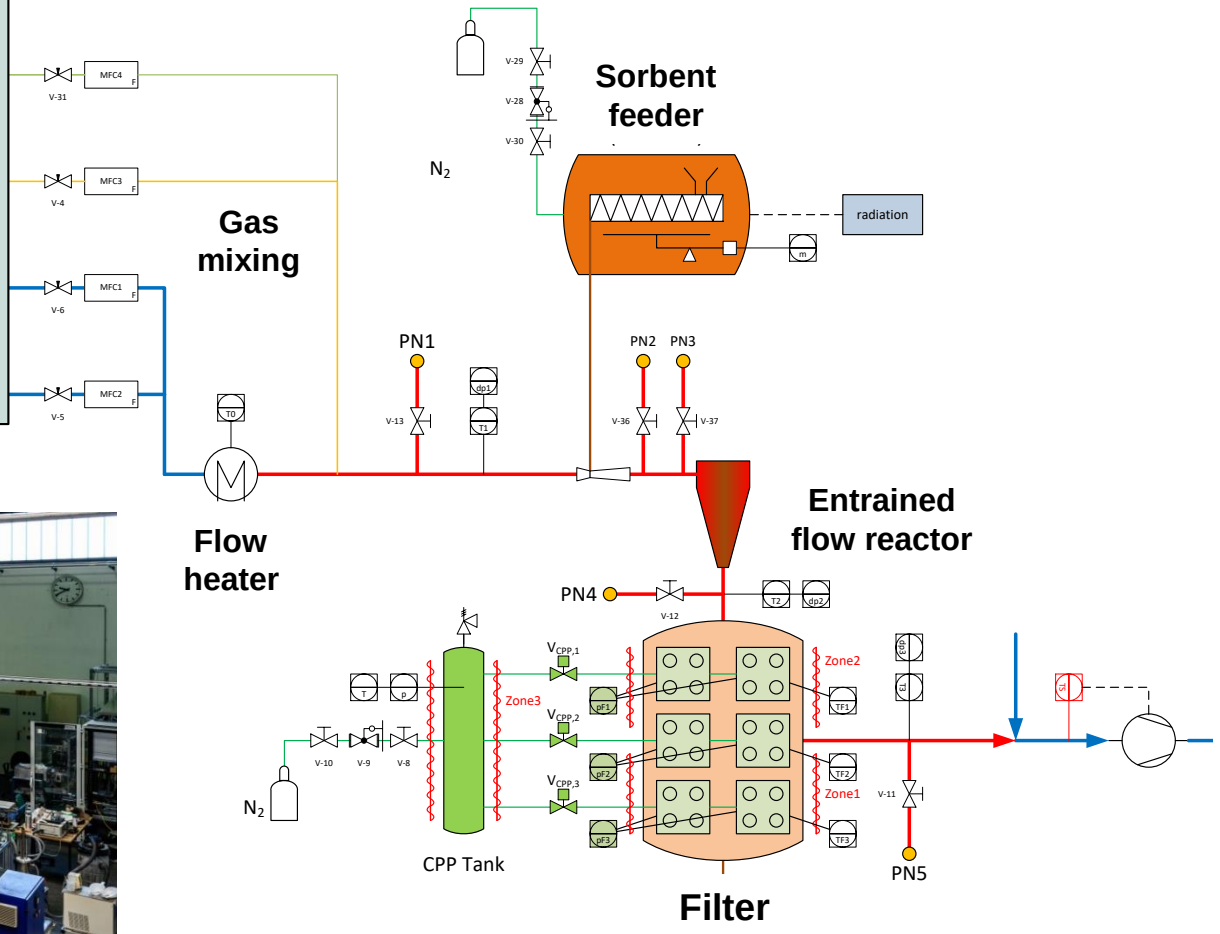


CALIDA

Combined HT filtration and entrained flow sorption facility

Technical Data

Volume flow	123 m³/h (30 m³/h STP)
Temperature	max. 850 °C
24 Filter elements	L 400 mm d_a 60 mm
Filter area	1.8 m²
CPP recleaning	N_2



Summary and outlook

- ✓ The bioliq dry HTHP syngas cleaning process chain provides specified syngas for the most relevant trace contaminants.
- ✓ The conversion of N-species in a catalytic step is still to be done
- ✓ Development of an entrained flow sorption process for trace contaminants.
- ✓ Basic investigations on sorption kinetics of the most critical H_2S on mineral Na and Ca sorbents reveal a strong influence of temperature.
- ✓ Na based sorbents show the fastest H_2S sorption kinetic.

- ➢ Detailed investigation on the sorption process during entrained flow sorption. at PDU CALIDA will provide design parameter for the bioliq process.
- ➢ Investigations on CuO based sorbents for HT polishing filters are ongoing.
- ➢ Catalytic impregnation of ceramic fiber filters are under development.

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MUT ADVANCED HEATING

PALL Pall Corporation