

Trockene Synthesegasreinigung bei hohen Temperaturen

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Kolloquium

Sustainable BioEconomy

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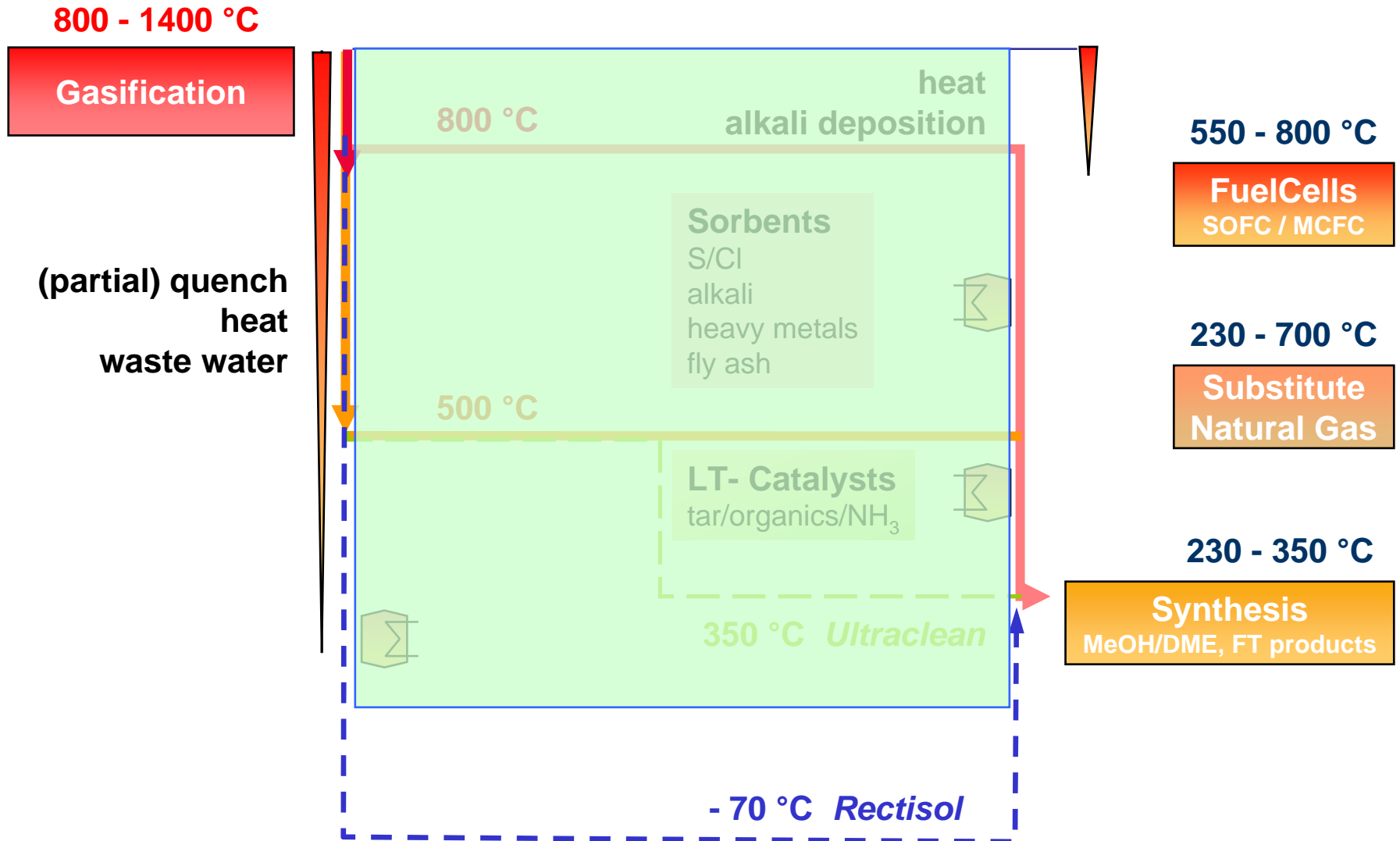
- **Synthesegasreinheit - Relevante Spurenstoffe - Anforderungen?**
- **Stand der Technik**
- **Trockene HT-Synthesegasreinigung - Welche Anforderungen?**
- **HT - Sorption**
- **HT - Partikelfiltration**
- **Katalytische Reinigung**
- **Gasreinigungslinie am Pilotvergaser REGA**
- **Konzept für integrierte HT Syngasreinigung**
- **Schlussfolgerungen/Ausblick**

mg/Nm ³	Biomass gasification	Gas motor ¹	Gas turbine	FT (Sasol)	MeOH ¹
Particles	10 ⁴ - 10 ⁵	< 50	< 1	n.s.	0.2
Tar	0 - 20 000	< 100	< 5	n.s.	< 1
Alkali	0,5 - 5	n.s.	< 0,2	< 0.01	< 0.2
NH ₃ , HCN	200 - 2000	< 55	n.s.	< 0.02	< 0.1
H ₂ S, COS	50 - 100	< 1150	< 1	< 0.01	< 0.1
Halogens	0 - 300	n.s.	< 1	< 0.01	< 0.1

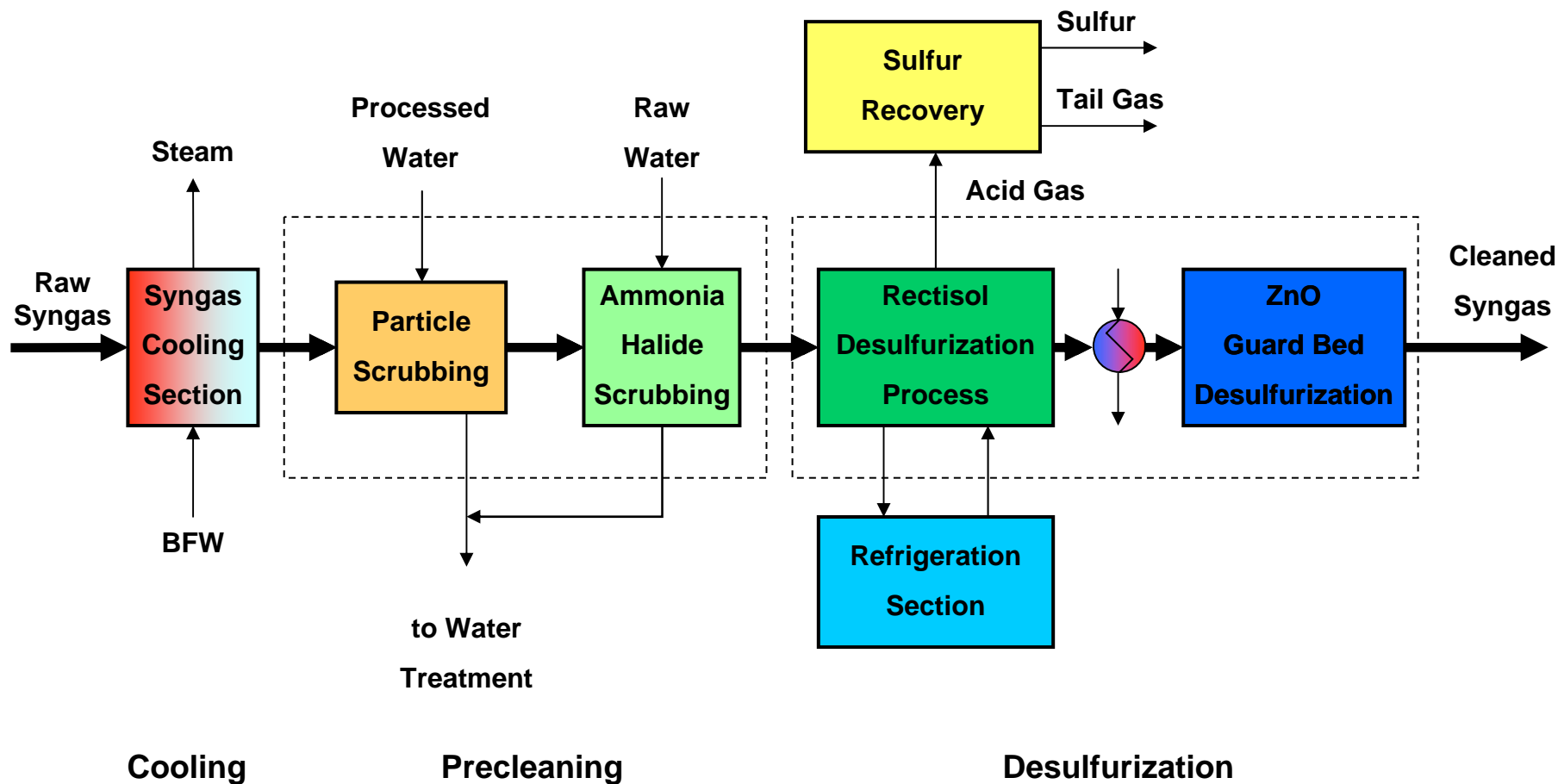
n.s. not specified

Zuberbühler 2004, ¹Köppel 2007

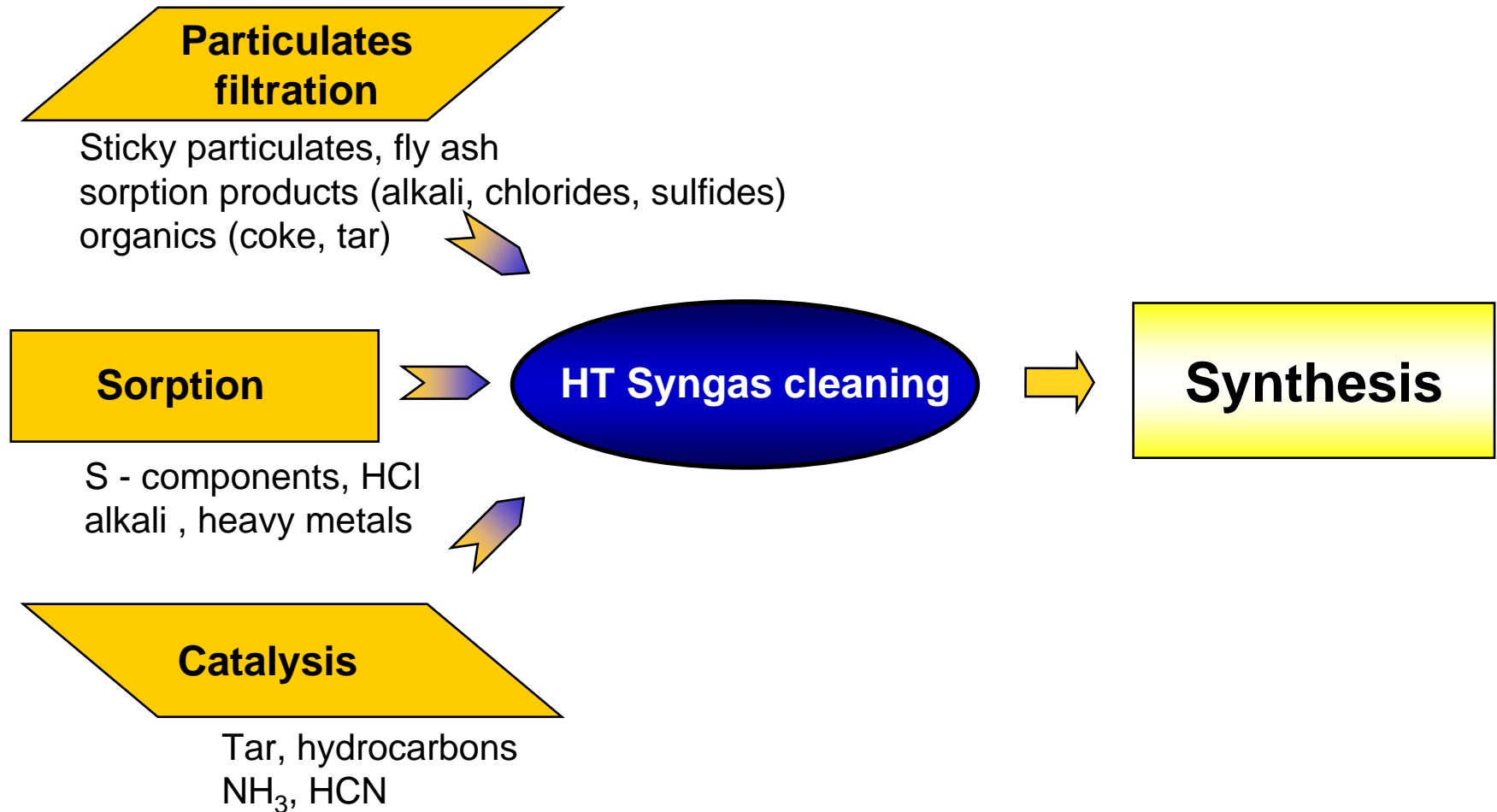
Syngas cleaning for HTHP utilization



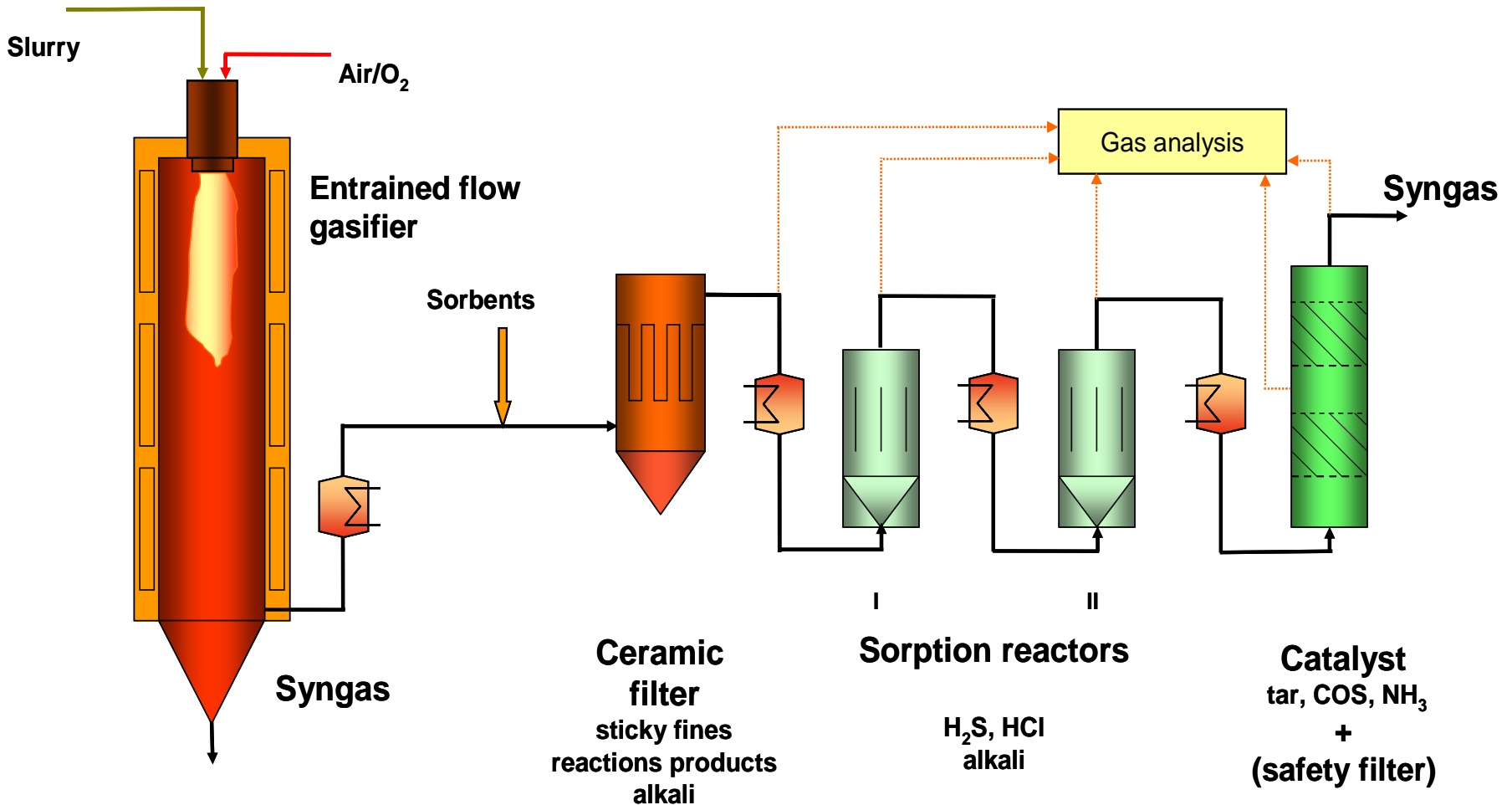
- ✓ Methanol (-75 °C bis -20°C)
 - ✓ Polyethylenglycol-dimethylether
 - ✓ N-methyl-2-pyrrolidon [NMP] (bis 20 °C)
 - ✓ Propylencarbonat
 - ✓ N-formylmorpholin [NFM]
 - ✓ Oligo-ethylenglycol-methyl-isopropyl-ether
 - ✓ N-Methyl-caprolactam (NMC)
- Rectisol**
- Selexol**
- Purisol** Lurgi
- Fluor solvent process**
- Morphysorb**
- Sepasolv** (MPE)-BASF
- VEB Leuna**
- + Chemical sorbents, typically amines or carbonates (MEA, aMDEA)



- Nasswäschen sind Standardverfahren für Methanol- und FT-Synthese
 - Für alle relevanten Schadstoffe werden die spezifizierten Reingaswerte erreicht.
 - Produkte: Schwefel und CO₂
 - Problem: Aufwand und Kosten
 - Energiebedarf
 - Prozessdampfbedarf
 - Abwassermengen
 - Rectisolverfahren für $V > 100\,000\text{ Nm}^3/\text{h}$
- ➔ **HTHP Gasreinigung/- aufbereitung oberhalb Synthesebedingungen**
- Gesamtwirkungsgrad
 - Verfahrensvereinfachung
 - Kosten



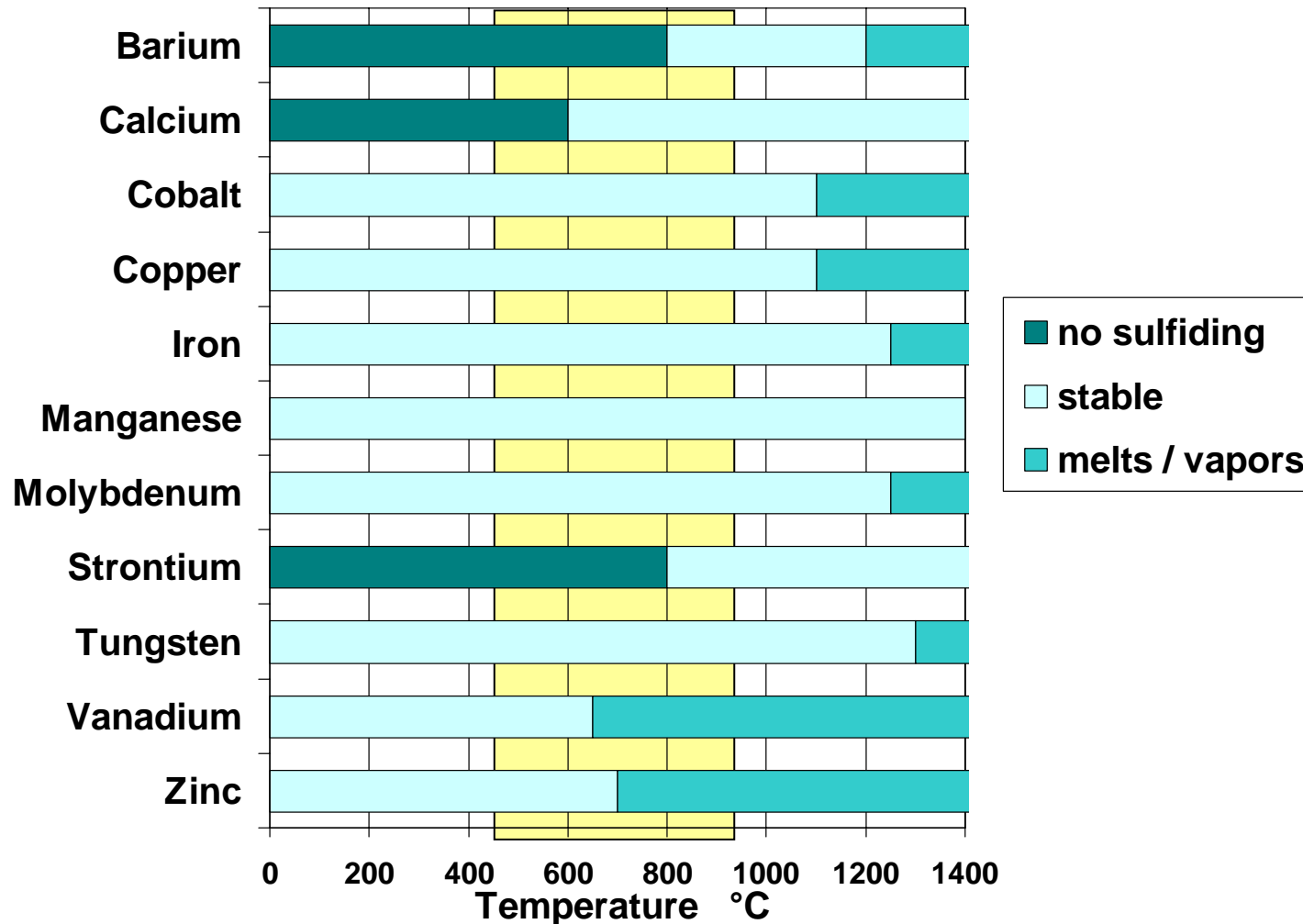
Entrained flow gasifier REGA with HT gas cleaning



REGA (Research Entrained Flow GASifier)

Sorption von sauren Gasen

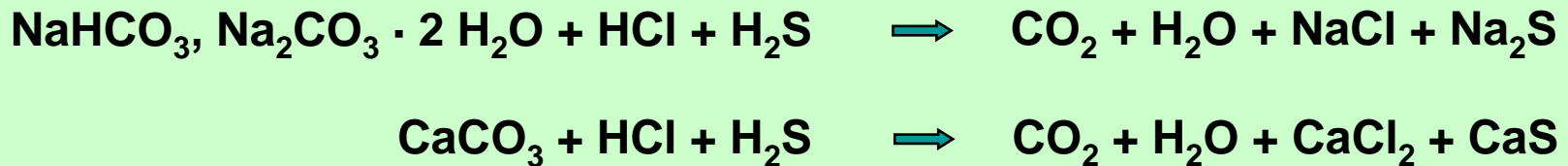
HT sorbents for S species



Westmoreland, Harrison 1976

HT sorbents and reaction products

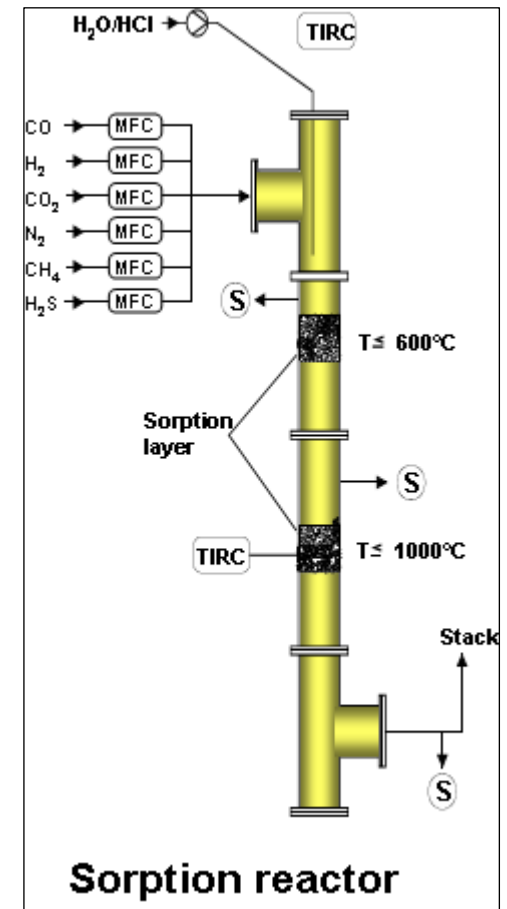
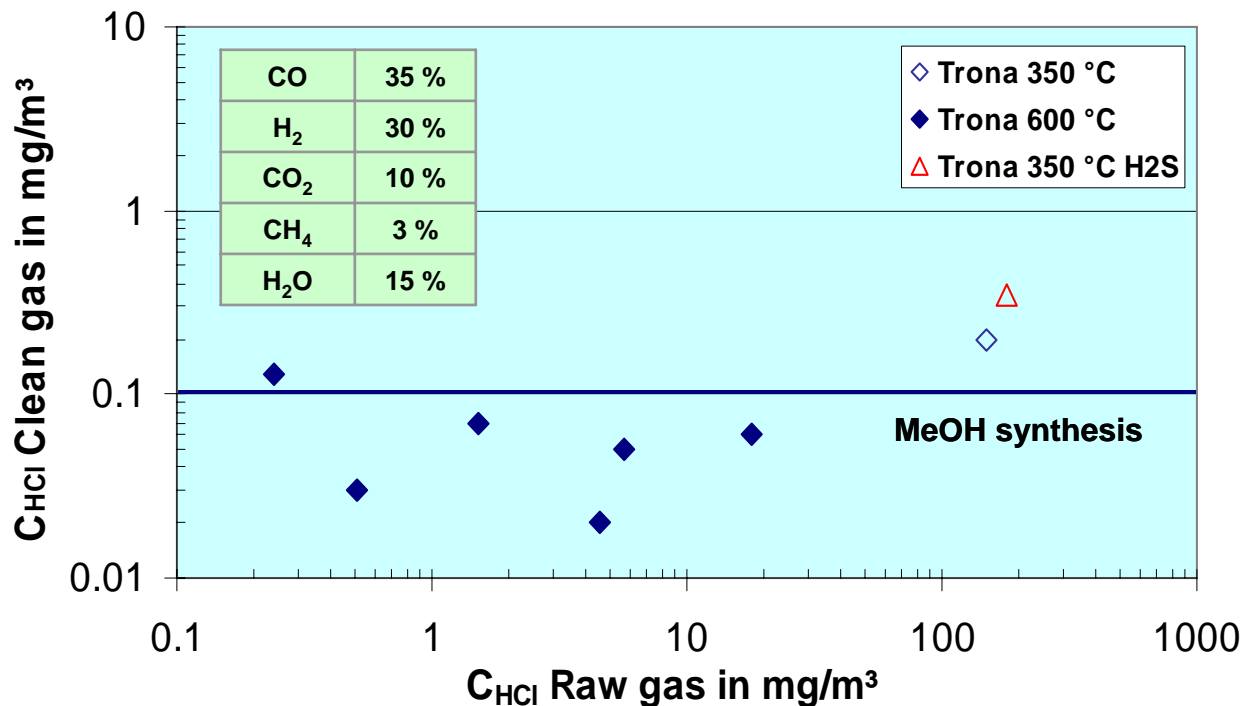
- Solid reaction products at process temperature (vapor pressure)
- Equilibrium on product side
- Low cost (natural) sorbents



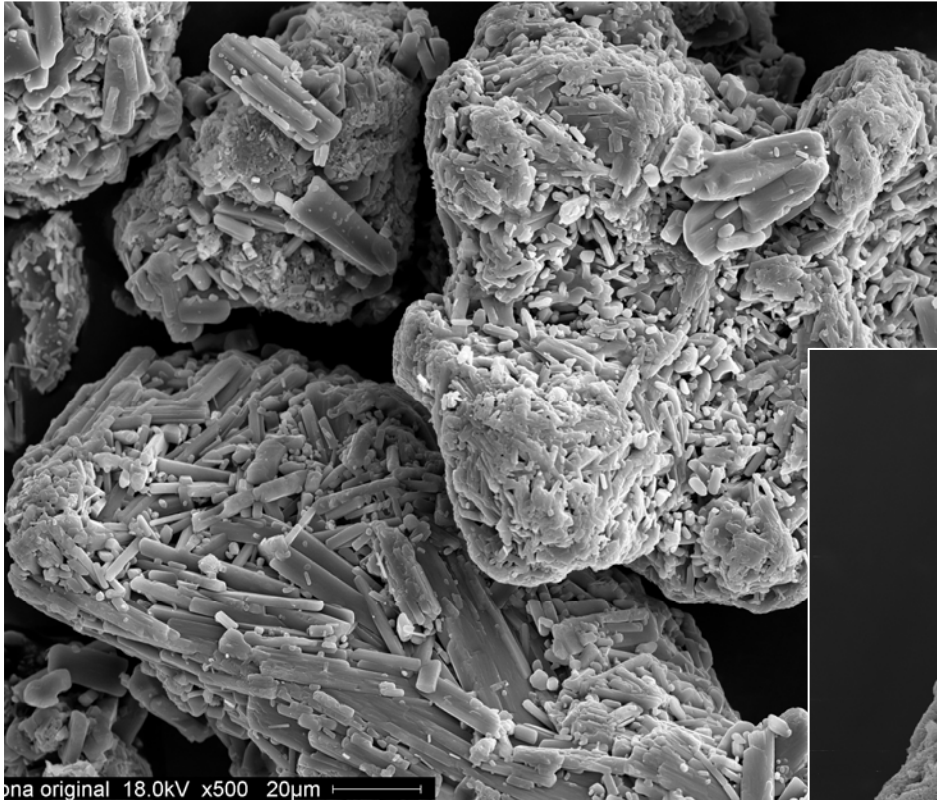
Na₂CO₃	851 °C		CaCO₃	825 °C
Na₂O	1132 °C		CaO	2572 °C
NaCl	801 °C		CaCl₂	772 °C
Na₂S	1180 °C		CaS	845 °C

Melting points
sorbents
reaction products

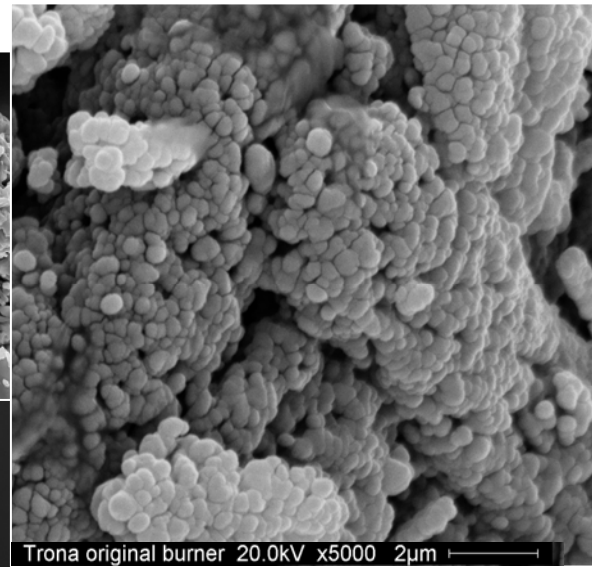
- Trona mineral (NaHCO_3 , $\text{Na}_2\text{CO}_3 \cdot 2 \text{H}_2\text{O}$)
- Sorption in fixed bed $H = 70 \text{ mm}$, $t_{\text{Res}} = 2 \text{ s}$
- Temperature range $350 - 600 \text{ }^\circ\text{C}$
- Sampling in H_2O , KOH , Ion chromatography analysis



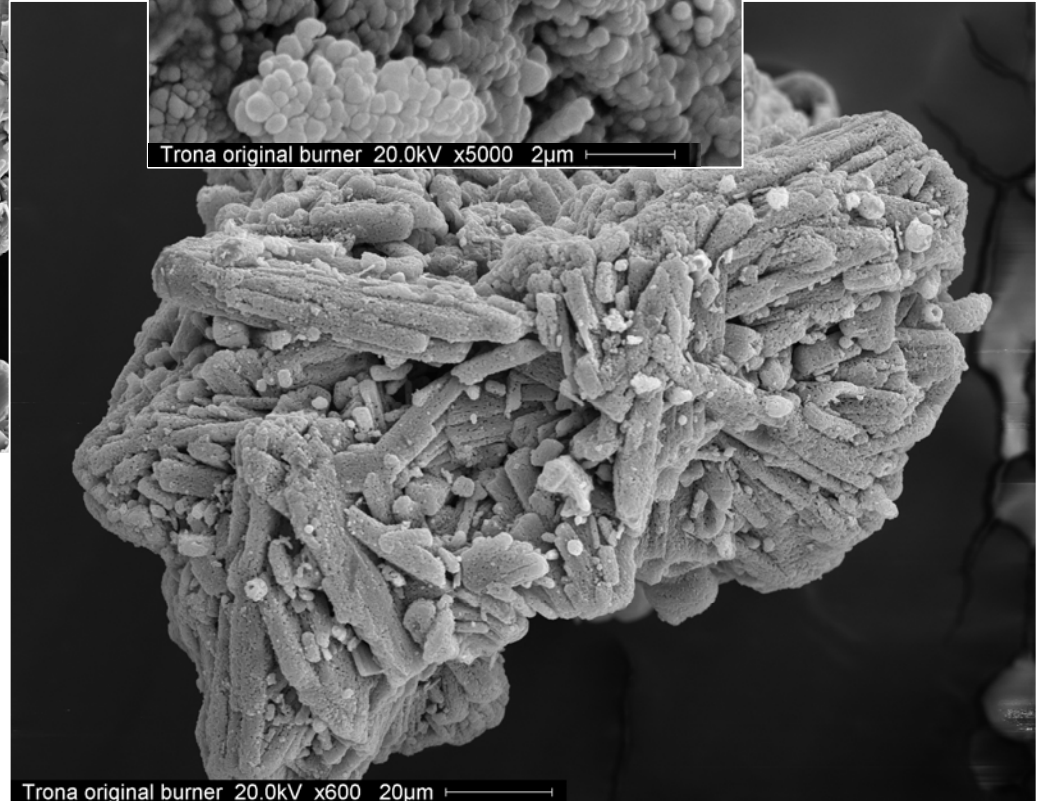
Sorbent Trona



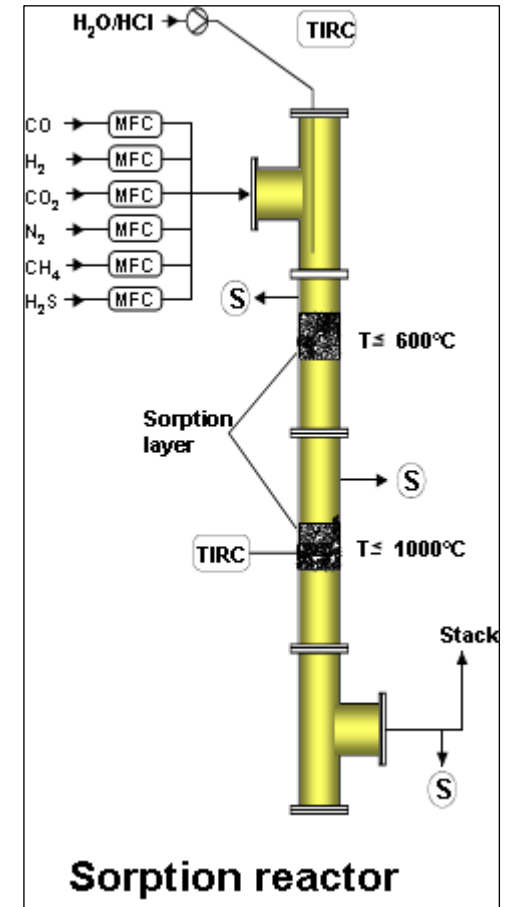
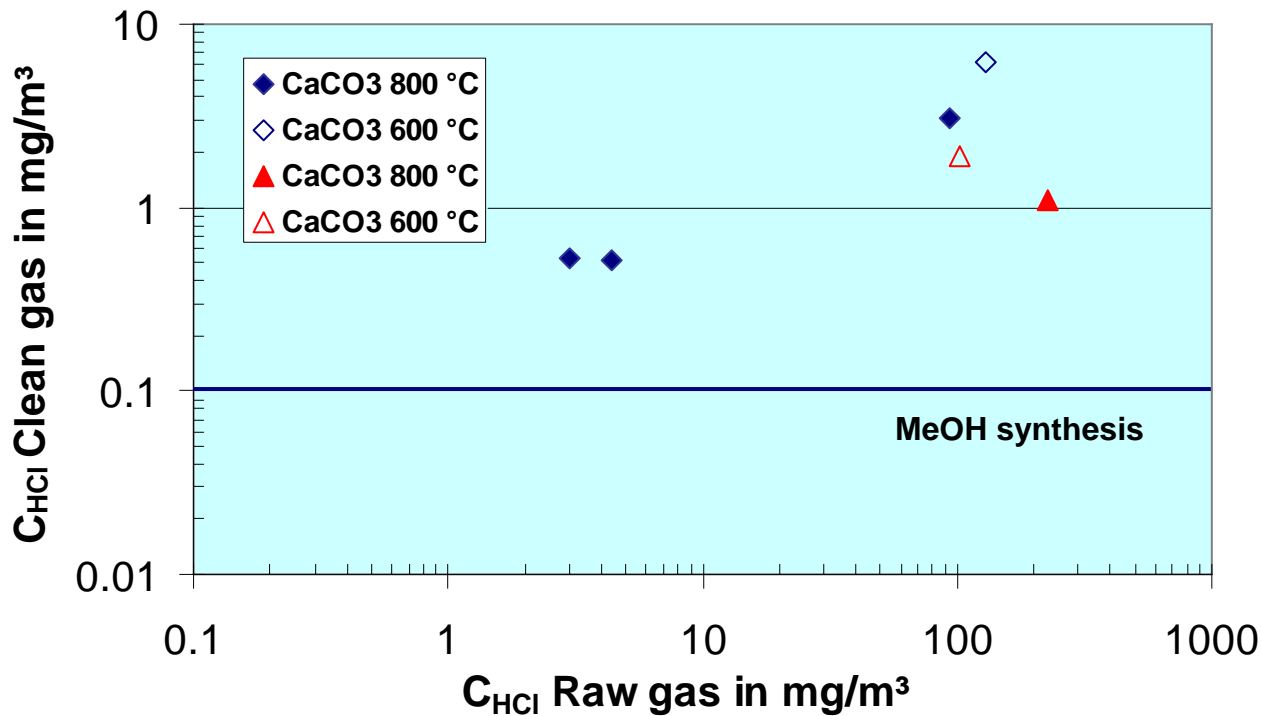
unconditioned Trona particles



Trona particle
tempered

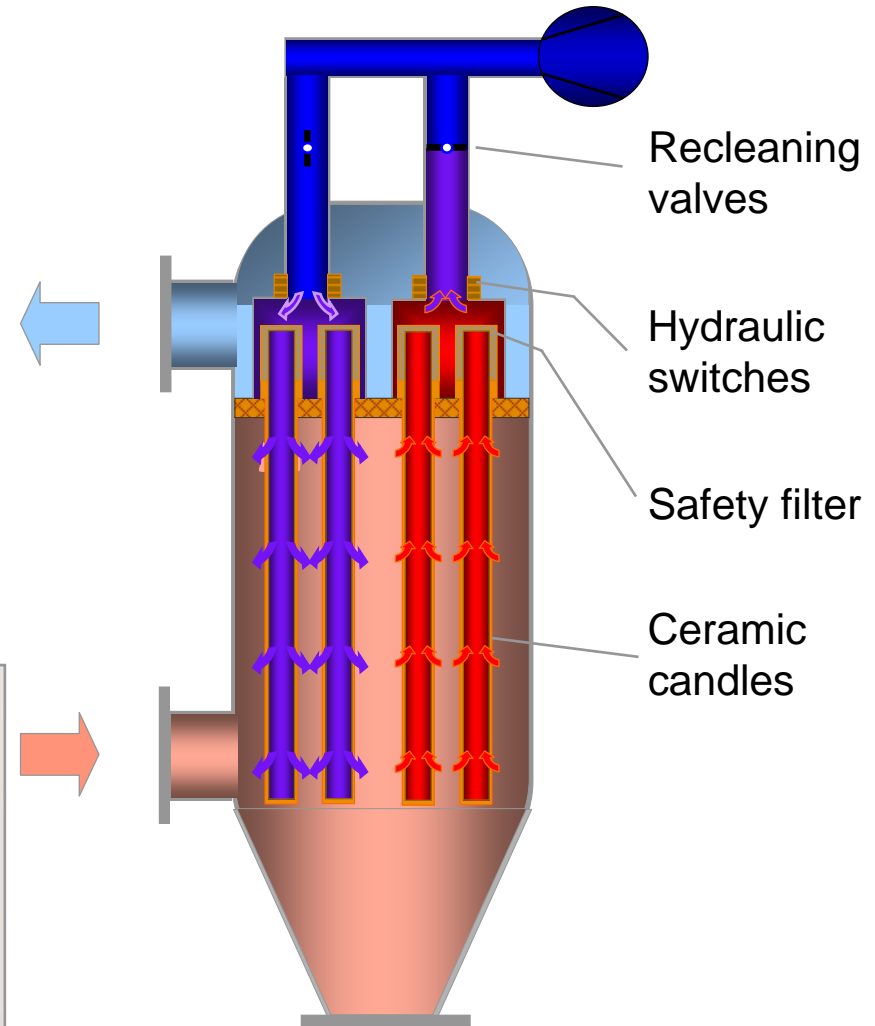
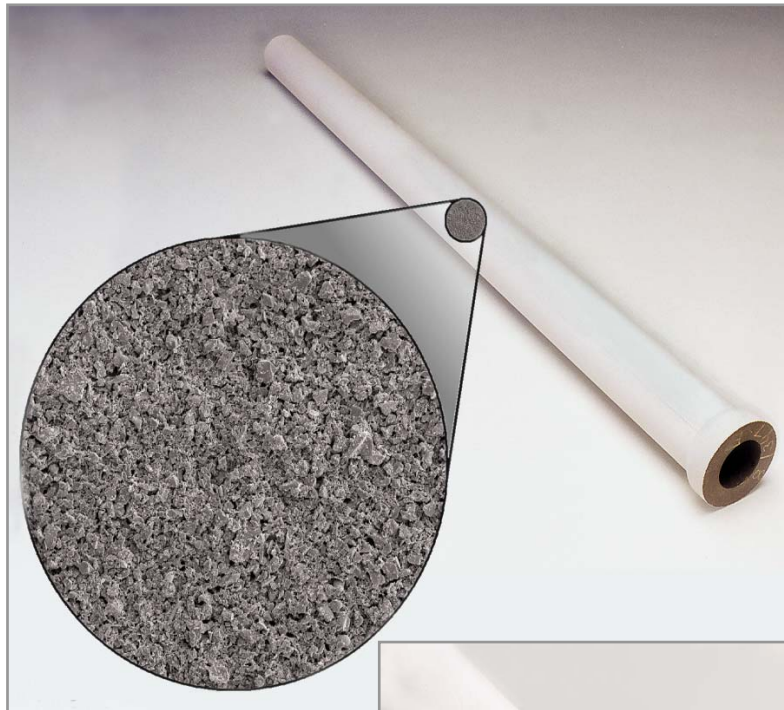


- CaCO₃, particle size ~ 15 μm
- Sorption in fixed bed H 70 mm, t_{Res} = 2,4 s / 2 s
- Syngas composition CO 35 %, H₂ 30 %, CO₂ 10%, H₂O 15 %
- Sampling in H₂O, KOH, Ion chromatography analysis

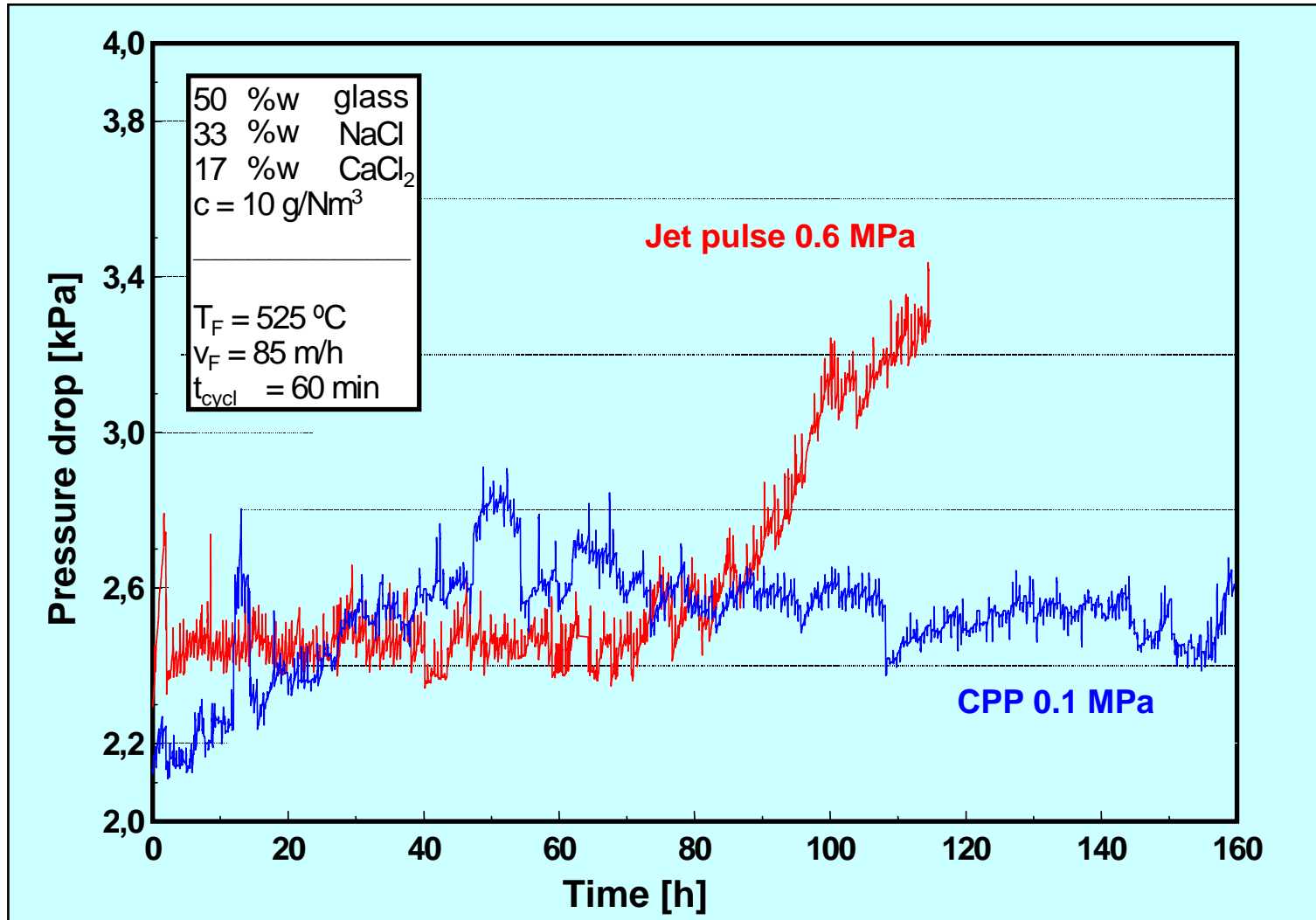


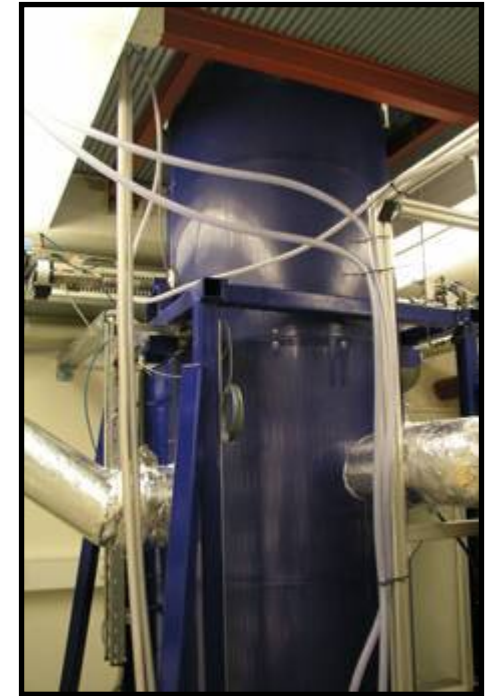
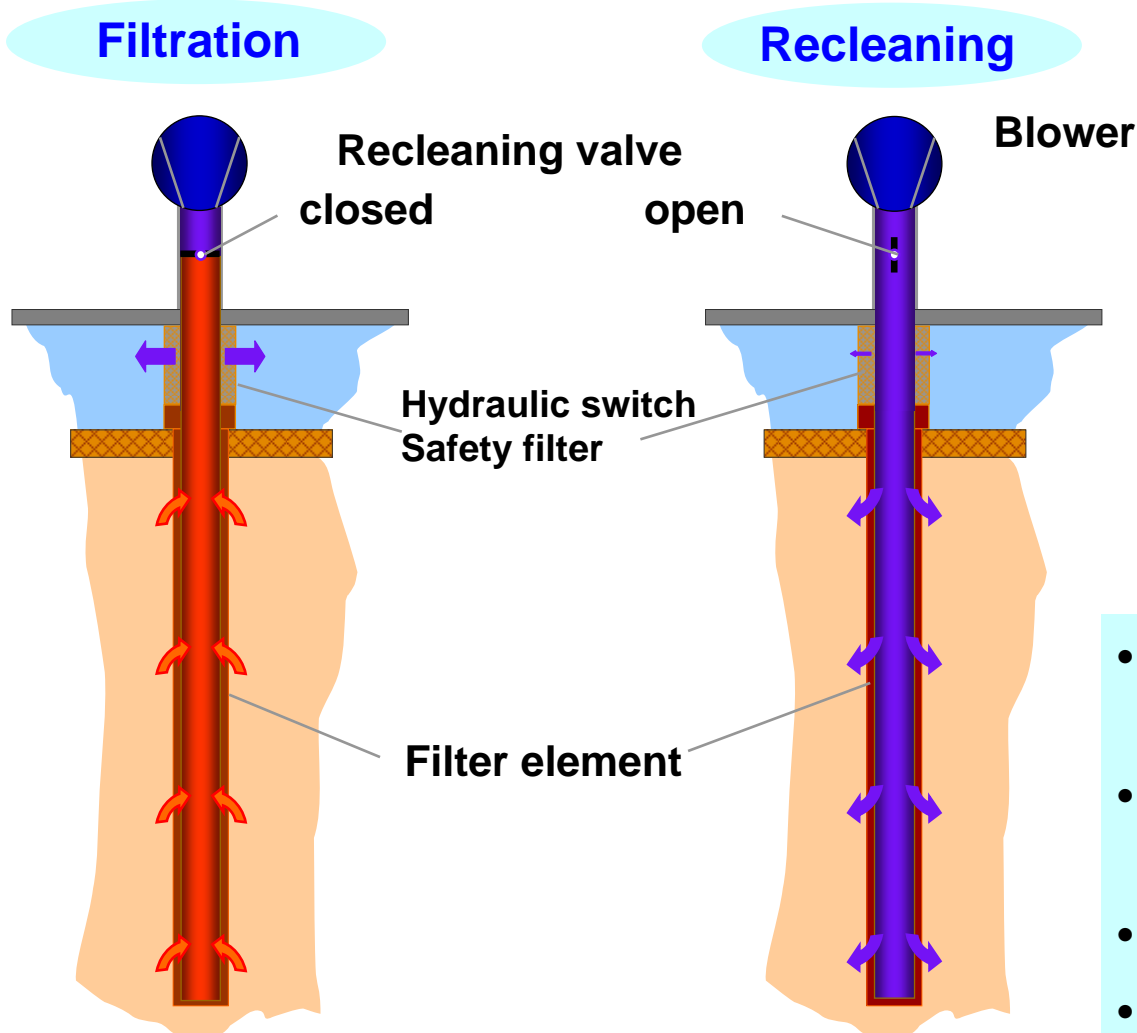
Partikelfiltration

Ceramic filters



Filtration of eutectic NaCl/CaCl₂ mixture





- Adaptation of the recleaning intensity to the dust properties
- Loading pressure is low, independent from system pressure
- No interference of the dust load
- Fail-safe system integrated

Katalytische Konversion

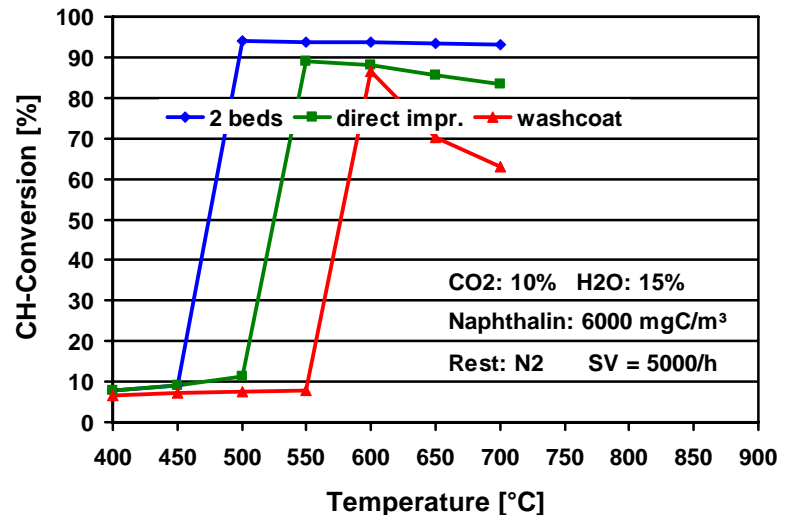
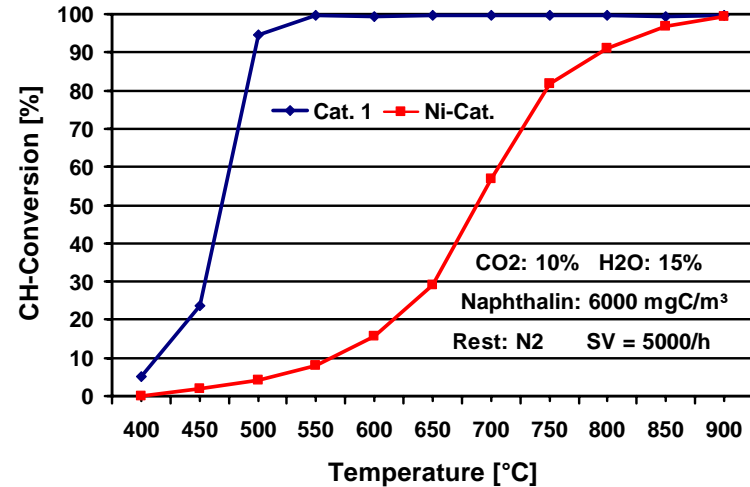
Challenge

- LT catalysts for tar conversion
- Coke formation / deactivation
- Catalysts pollution by S, Cl, N, alkali components

R&D

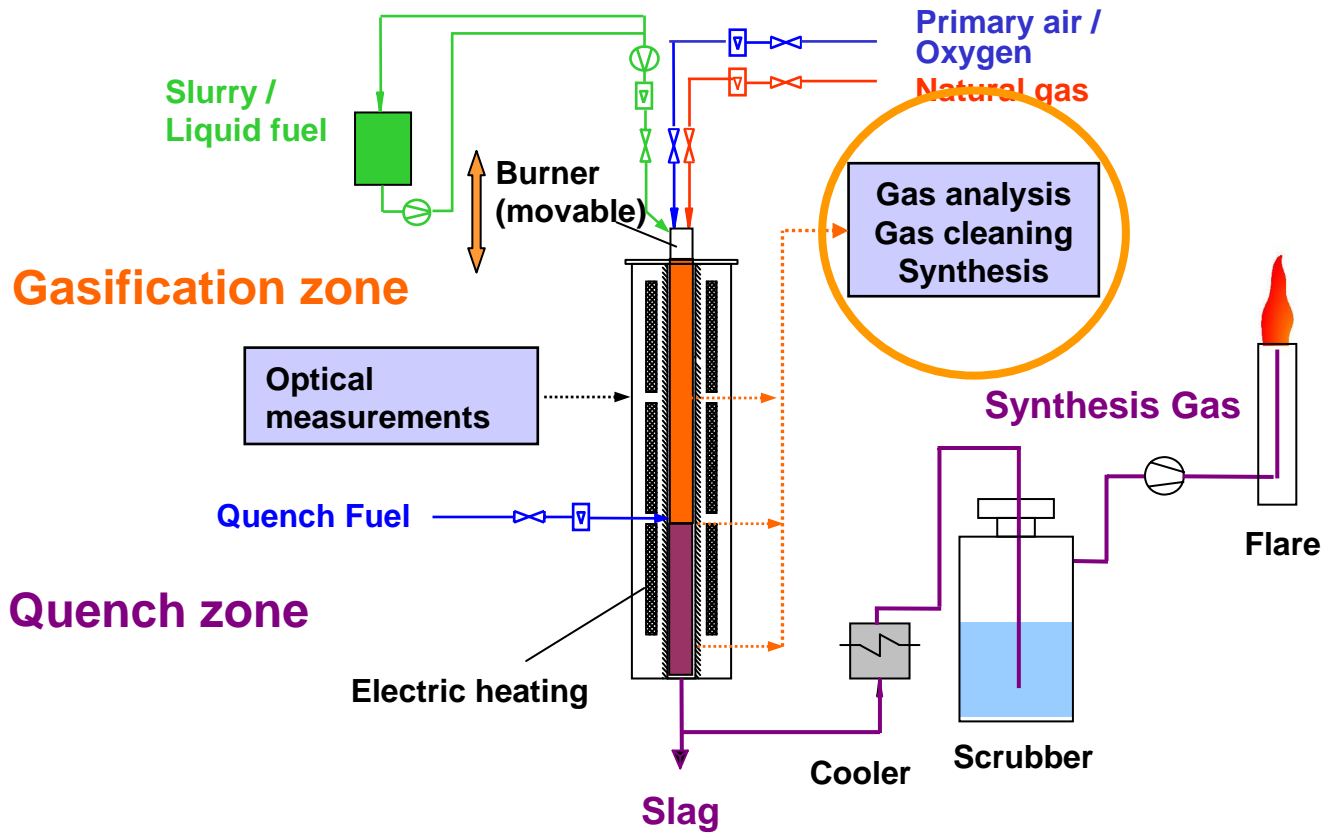
- Development of LT catalysts
⇒ to operate gas treatment at uniform temperature niveau
- Performance of Ni-based HT catalysts
⇒ to improve regeneration and S-sensitivity
- Combination with particle filtration
⇒ to integrate processes

Results



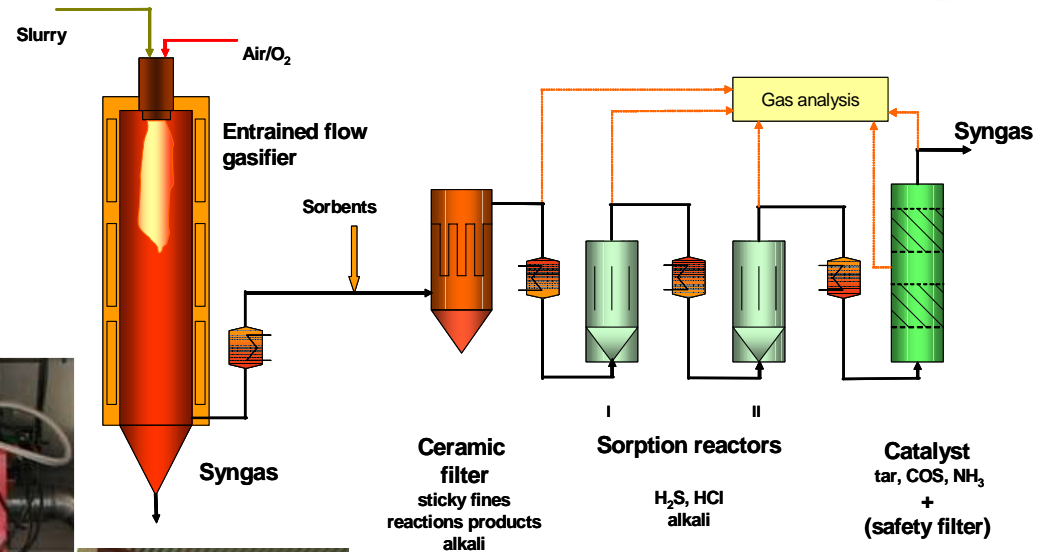
Gasreinigungslinie am Pilotvergaser REGA

REGA (Research Entrained Flow GASifier)



Refining Biomass - HT Syngas Cleaning REGA

- Raw syngas $< 10 \text{ Nm}^3/\text{h}$
 $T < 800 \text{ }^\circ\text{C}$
- Dry HT syngas cleaning processes at temperatures (300 - 800 $^\circ\text{C}$)
- Entrained flow sorption upstream ceramic filter
- Ceramic filter
 - 3 candles
 - filter area 0.25 m^2
 - CPP recleaning (N_2)
- Fixed bed reactors (2x)
 - $t_{\text{res}} < 2 \text{ s}$
 - $\text{Ø } 150 \text{ mm}$
 - H 150 - 300 mm
- Catalyst beds (2x)



isifier



Ceramic filter

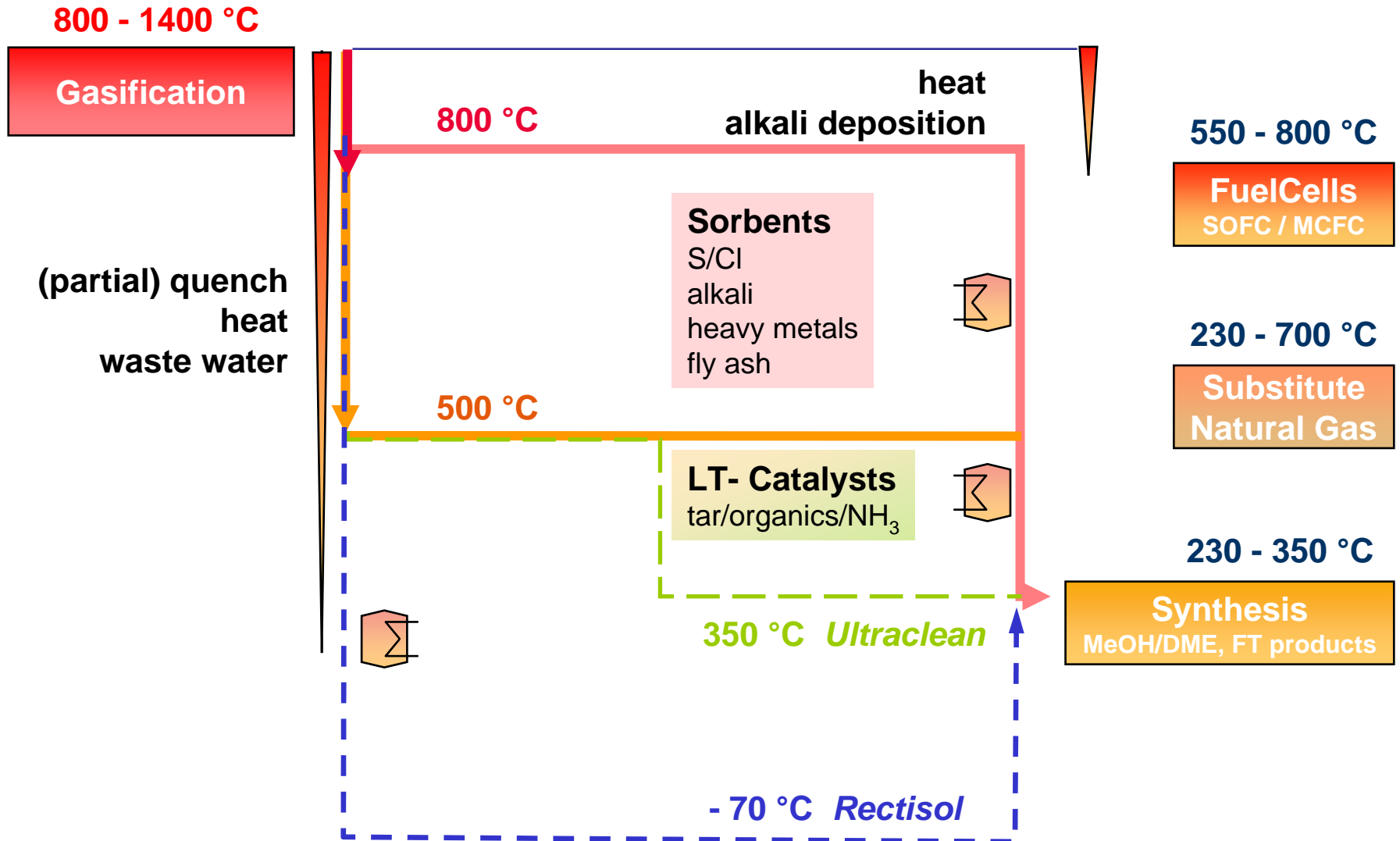


Sorption reactors

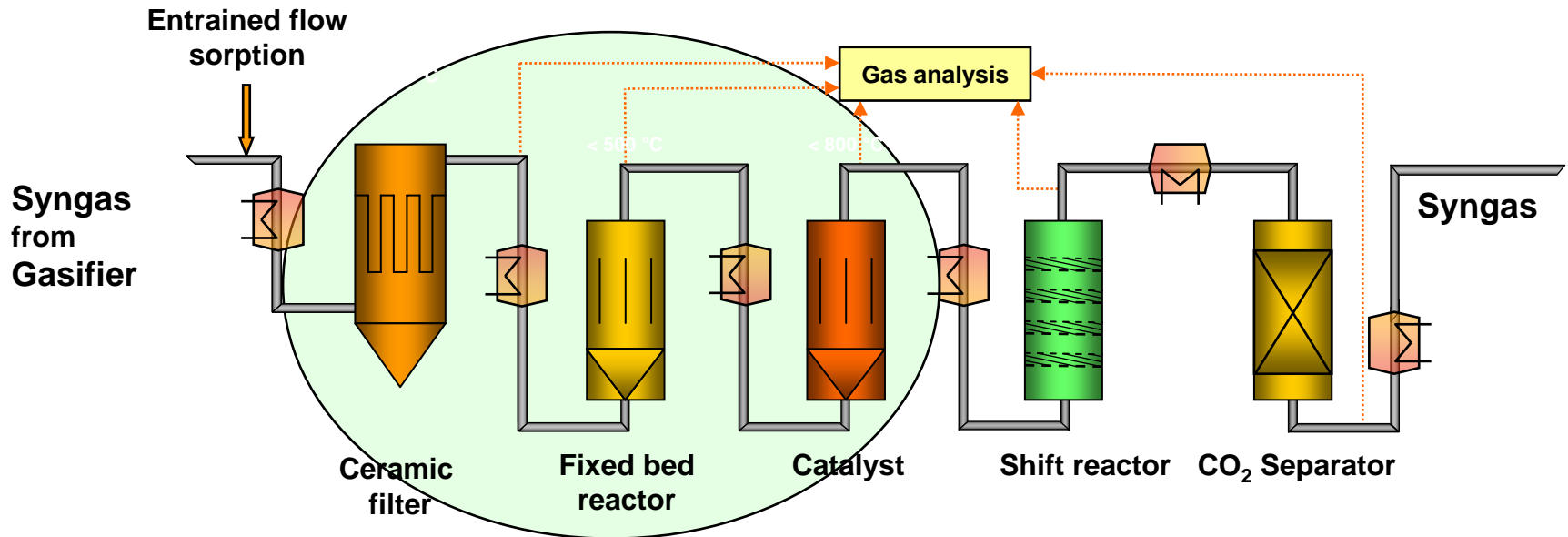
Catalyst

REGA Research Entrained Flow GASifier)

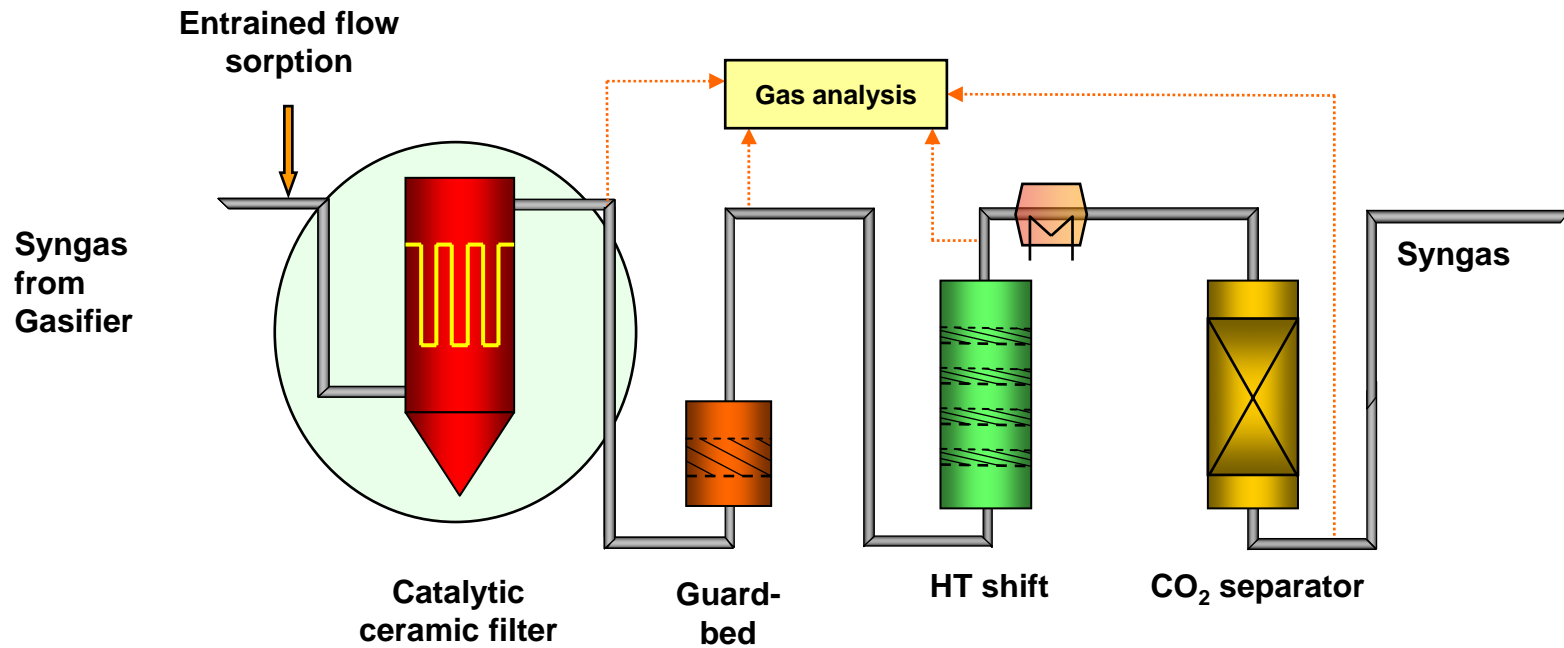
Syngas cleaning for HTHP utilization



Basis for HTHP syngas cleaning **bioliq**



HTHP Syngas cleaning - integrated



- Durch die trockene HT-Syngasreinigung kann die Effizienz des Gesamtprozesses gesteigert werden.
- Reinheitsgrade für Methanolsynthese mit HT- Sorbentien sind auf Basis mineralischer Sorbentien erreichbar.
- Backende oder klebrige Flugaschen und Sorptionsprodukte können durch HT Filtration mit keramischen Filtermedien abgeschieden werden.
- Entwicklung von NT Katalysatoren erlaubt Absenkung der Temperatur für die Teerspaltung.
- Systemerprobung mit biomassestämmigen Syngasen
- Entwicklungsbedarf besteht hinsichtlich Integration der Reinigungsstufen für alle relevanten Spurenstoffe.
- Spurengasanalyse für relevante Species und zur Prozesssteuerung