Sorbent-based final gas clean-up

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Final gas cleaning
Targets

Impurities (ppm_v)	Fluidized bed gasification (steam), post-filtration+reforming		Purity requirement (FT cat.)	
	Woody-residues	Agro-residues	Leibold et al. (SASOL)[1]	Boerrigter et al.[2]
H_2S	20 - 200	40 - 400	< 0.01	< 1
COS	2 - 20	1 - 40		
HCN	0.5 - 5	1 - 10	< 0.02	< 1
NH_3	50 - 500	100 - 1000		
Halides	< 2	< 5	< 0.01	< 0.01
Alkalis	< 1	< 1	< 0.01	< 0.01
Tars	< 100	< 200	Below dew point	Below dew point

- Catalytic synthesis: Strict gas purity requirements

1 Leibold et al.https://doi.org/10.1016/j.powtec.2007.05.012
2 H. Boerrigter et al. Green Diesel from Biomass via Fischer-Tropsch synthesis: New Insights in Gas Cleaning and Process Design, Pyrolysis Gasif. Biomass Waste, Expert Meet. (2002)

Final gas cleaning

Challenges:

- Deep removal requirement
- Multicontaminant gas composition
- Varying concentrations due to biomass heterogeneity

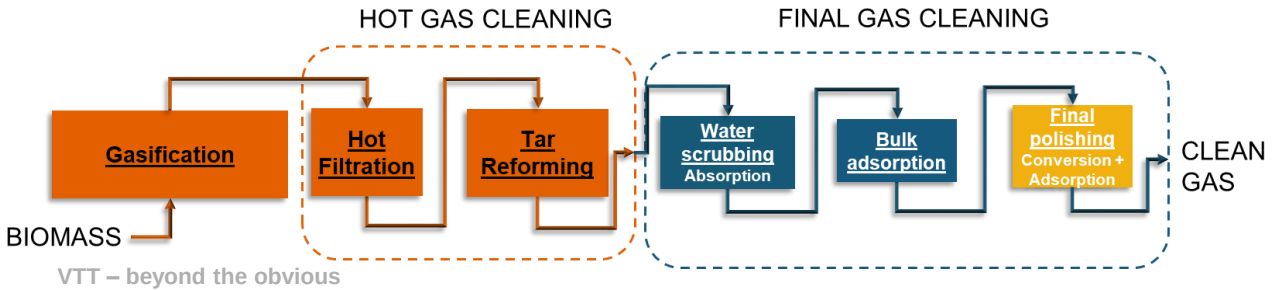
Conventional gas cleaning solutions:

- Solvent scrubbing methods
- Rectisol/Selexol-type absorption processes don’t ”downscale” well
  → up to 20+ % of BtL plant total CapEx

Low-CapEx cleaning concept

- Contaminant removal by dry-bed adsorption and organic solvent-free scrubbing
- Over 20 % lower CapEx and OpEx to conventional wet-scrubbing solutions

- Tailored for biomass-specific gas impurity matrix/levels
- Raw syngas relatively ”clean” due to optimized hot gas cleaning → Simpler final gas cleaning technically/economically viable
- Optional selective CO_2 removal by pressurized water scrubbing
  - 50 – 80 % CO_2 removal rate



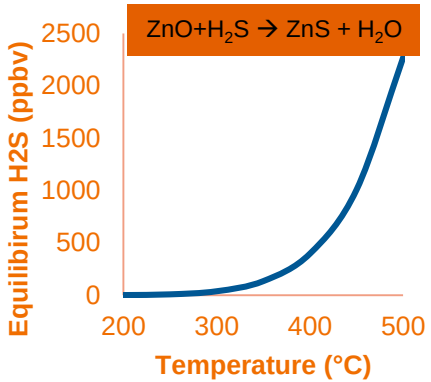
Adsorbent materials

Metal Oxides

$$MeO_x(s) + xH_2S(g) \rightarrow MeS_x(s) + xH_2O(g) \qquad \Delta H_r < 0$$

- ZnO capable of adsorbing inorganic compounds
  - Requires elevated temperatures, > 200 °C, to be effective

Oxide	Cost ($/kg)
Fe_2O_3	< 0.5
TiO2	1-3
ZnO	1-3
CuO	4-10
MnO	4-10
ZrO_2	4-16
NiO	6-10
CoO	14-20
CeO	16-20
Cr_2O_3	16-20
MoO_3	16-20

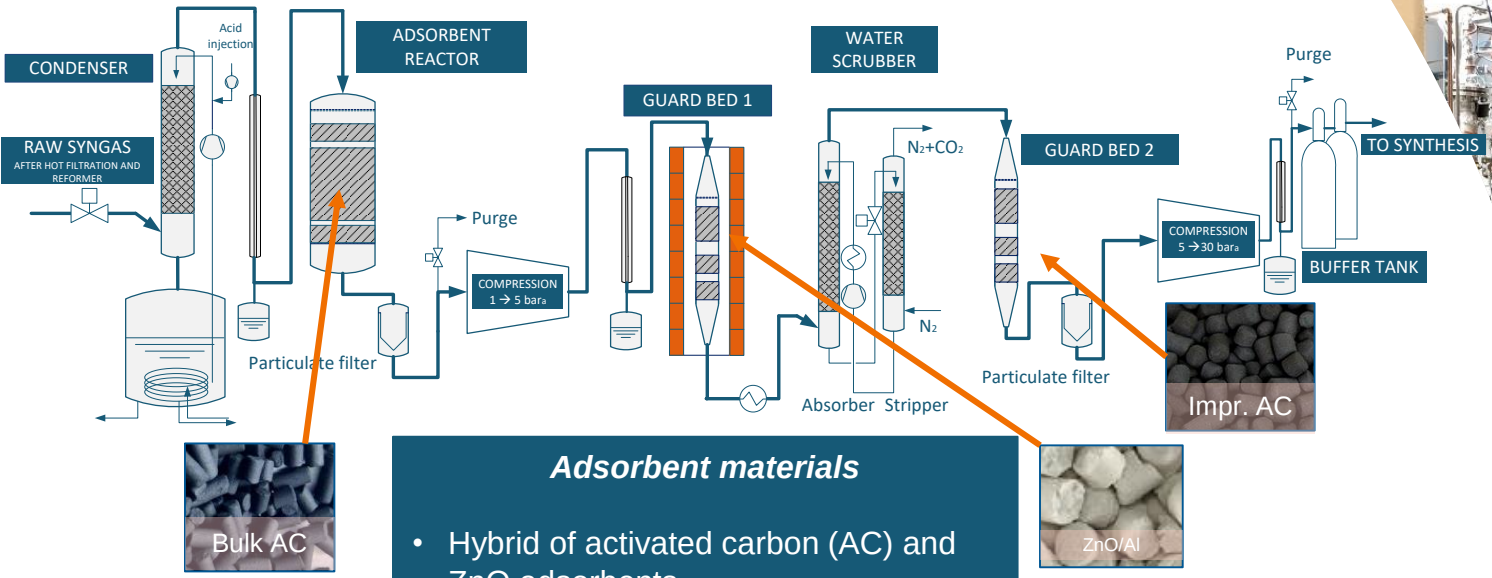


Activated carbons (AC)

- ACs can adsorb both organic and inorganic compounds
  - Active at low temperatures (< 100 °C)
  - Oxidative H_2S removal identified as particularly effective:

$$H_2S + \frac{1}{2}O_2 \rightarrow \mathrm{S(s)} + \mathrm{H_2O} \qquad \Delta H_r < 0$$

PDU-Scale Final gas cleaning



Adsorbent materials

- Hybrid of activated carbon (AC) and ZnO adsorbents
- Dual function of ZnO-based adsorbent:
  - COS hydrolysis catalyst
  - H_2S adsorption

VALIDATION TEST RUNS FOR ENTIRE PROCESS; FROM GASIFICATION TO FT SYNTHESIS

Biomass → Gasification and hot gas cleaning → Final gas cleaning & compression → Intensified FT synthesis → 0.35-0.4 kg/h Syncrude

The projects have received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 727476 (COMSYN) and No 763919 (FLEXCHX).

Campaign results

- The final gas cleaning process achieved full removal of all analyzed syngas impurities in:
  - Woody-residue biomass
  - Agro-residue biomass
- Achieved syngas purity levels suitable for catalytic synthesis
- Demonstrated the feasibility of simplified final gas cleaning (when combined with optimized hot gas cleaning

	After hot gas cleaning	After final gas cleaning	
	Avg. (ppmv)	Max. (ppmv)	Avg (ppmv)
S-Species	90 - 340	0.3	<0.1/ 0
N-Species	270 - 720	0/b d	0/b.d
Halogens	n.a (1 - 5)	0/b.d	0/b.d
Metals	n.a	n.a	n.a
Benzene and tars (g/Nm^3)	0.2 - 0.4	0/b.d	0/b.d
Oxygen (vol %)	0	0/b.d	0/b.d

n.a not analyzed
b.d below detection limit

Conclusion

- Expensive wet-scrubbing gas cleaning technology replaced by adsorbent-based process
  - Tailored for biomass impurity profile
  - Economical at smaller scale

- Realization of process concept from idea to reality
  - Successful validation of gas cleaning process in full BtL configuration
  - Full removal of harmful species from real syngas

VTT

beyond

the obvious

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