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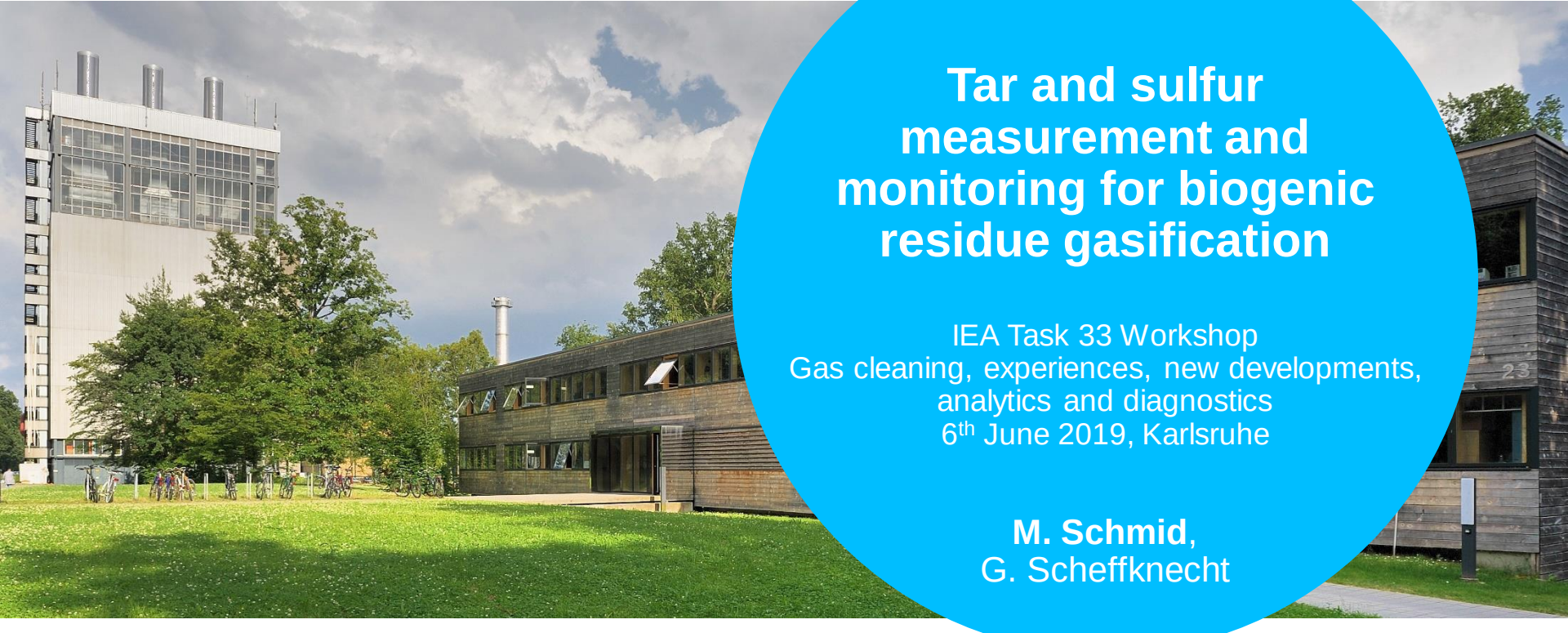

Tar and sulfur measurement and monitoring for biogenic residue gasification

IEA Task 33 Workshop
Gas cleaning, experiences, new developments, analytics and diagnostics
6th June 2019, Karlsruhe

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G. Scheffknecht

Agenda

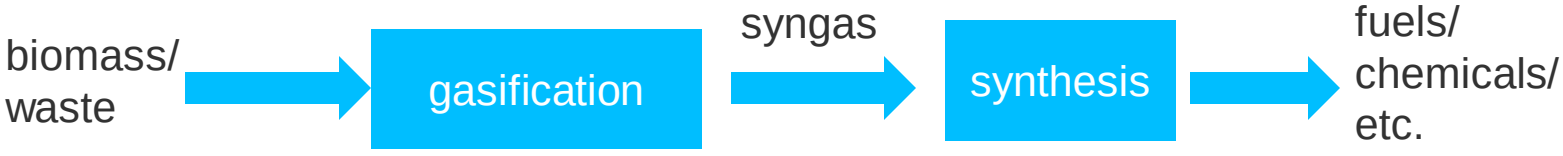
- gasification processes at IFK
- FID online tar analyzer TTA300
- sulfur measurement at IFK
- liquid tar sampling / tar protocol at IFK
- planned new online GC for tar and impuritiy measurement
- summary and conclusion

Motivation

- mitigation of climate change: to abandon the utilization of fossil carbon
- on contrast: continuing demand of carbon-based products
  - plastics, chemicals
  - fuels for transport (eg. kerosene), fuels for flexible heat and power production

→ utilization of carbon from biomass AND recovery of carbon from waste materials

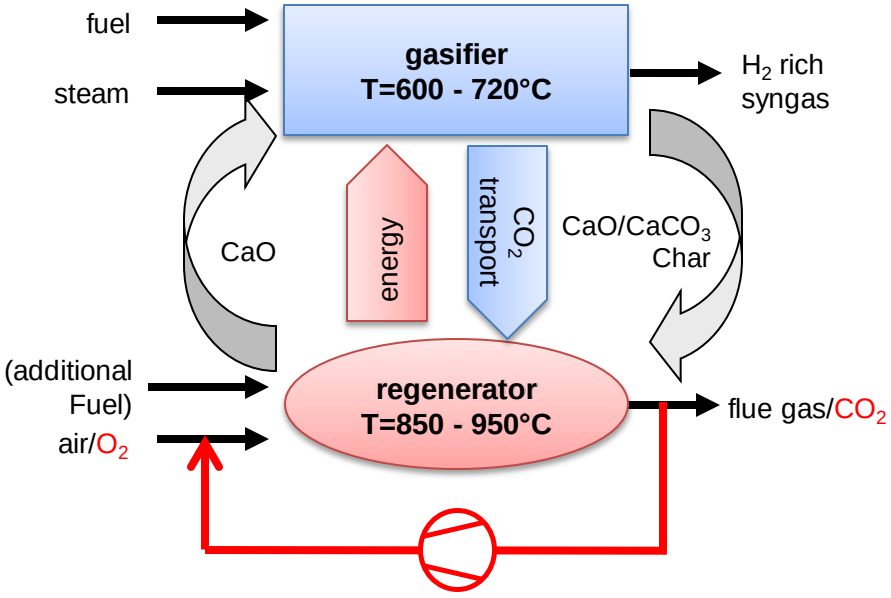
gasification as conversion process:



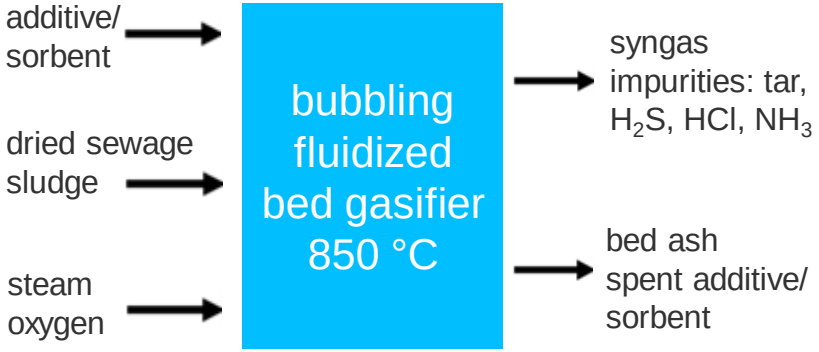
- Fluidized bed gasification → high efficiency, high feedstock flexibility
  - curent research at IFK:
    - sorption enhanced gasification (SEG)
    - steam-oxygen gasification

Fluidized bed Gasification Processes at IFK

SEG



Steam-oxygen gasification



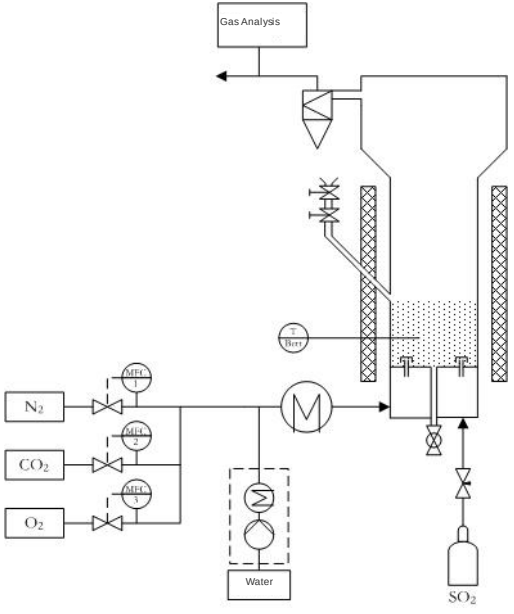
(Oxy-)SEG (Sorption Enhanced Gasifiaction)

- in-situ CO_2 capture: Limestone shifts CO_2 vom gasifier to regenerator
- H_2 rich and CO_2 lean syngas
- CO_2-rich off-gas for storage

- autothermal single bed gasification
- syngas suitable for synthesis
- applicable for high-ash containing fuels such as dried sewage sludge

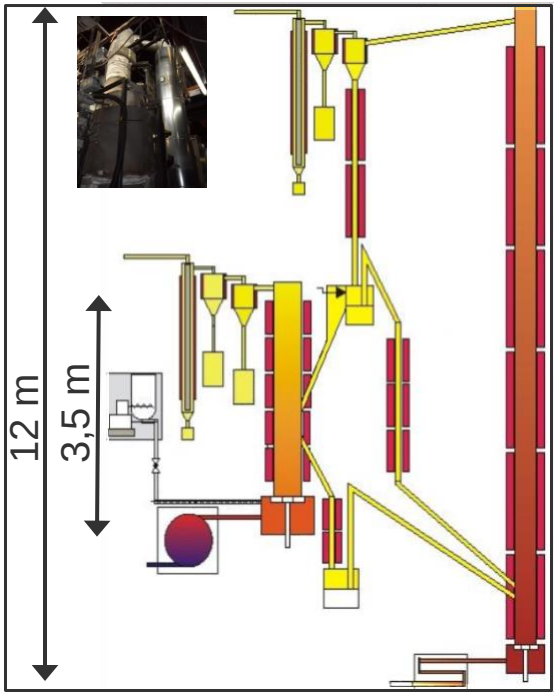
Fluidized bed research and pilot facilities (5-200 kW_{th})

1.5 kW_{th} (el. heated)



Height	0.65 m
Fuel rate	Up to 1 kg/h
Fluidization	BFB

20 kW_{th} (el. heated)



Height	3,5-12 m
Fuel rate	1-5 kg/h
Fluidization	BFB/CFB

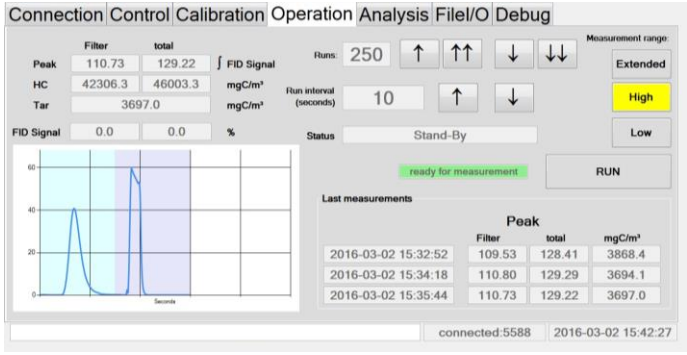
200 kW_{th} (not el. heated)

Height	6-10 m
Fuel rate	20-50 kg/h
Fluidization	BFB/CFB

FID Online Total Tar Analyzer TTA300

FID Online Total Tar Analyzer TTA300

produced by Ratfisch Analysensysteme



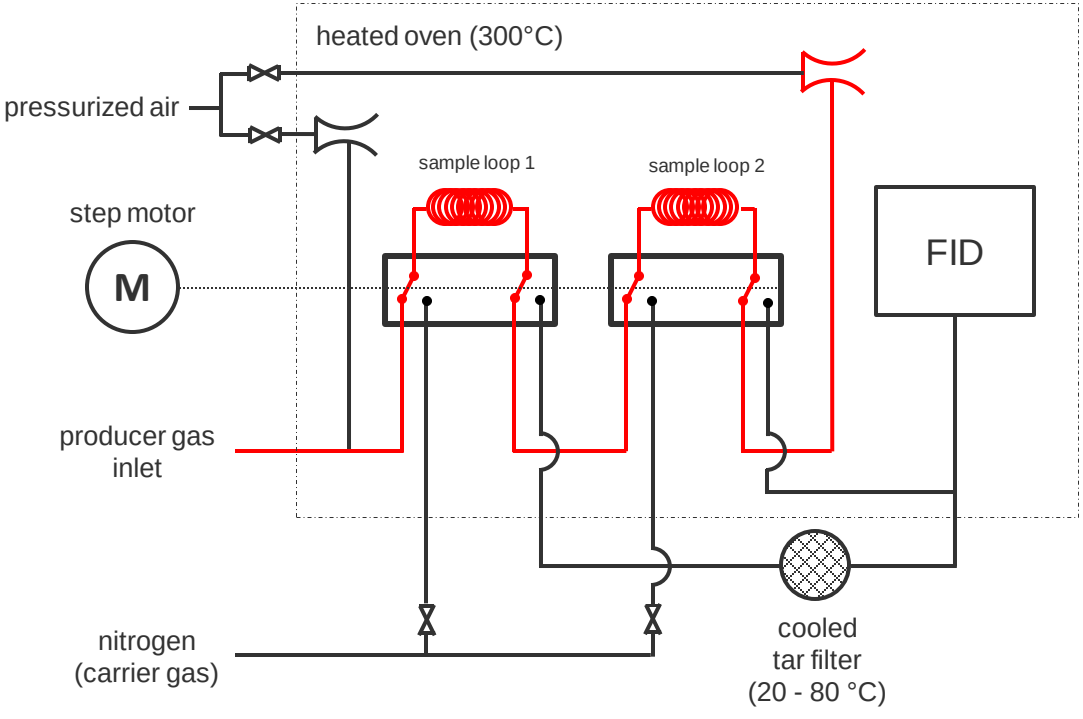
- measurement total tar concentration
- semi-continuous measurement every 1,5 min
- device operation temperature 300°C
- state of the art software and easy operation
- suitable for tar concentration > 1 g/m³

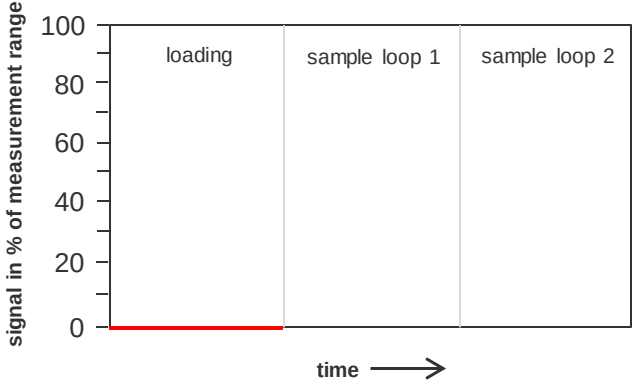
  → raw gas

- current status:
  - protoype at IFK is functional, but still requires frequent maintainance
  - design for low maintainance TTA300 device available at Ratfish
  - next step: production of first serial device

FID Online Total Tar Analyzer TTA300

Analyzer measurement principle – loading phase

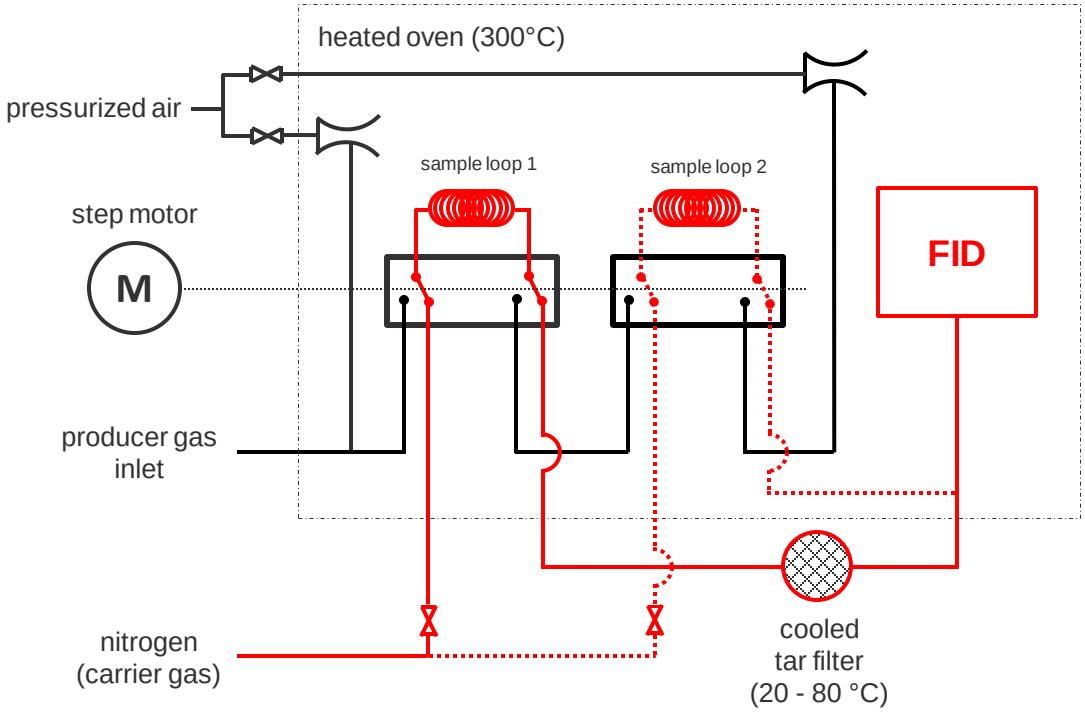


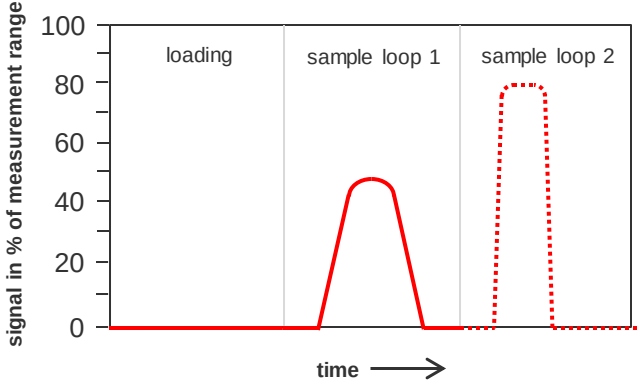


- Producer gas is sucked through sample loops via two venturi nozzles.
- Both loops filled successively.
- Detector signal is zero.

FID Online Total Tar Analyzer TTA300

Analyzer measurement principle – analyzing phase



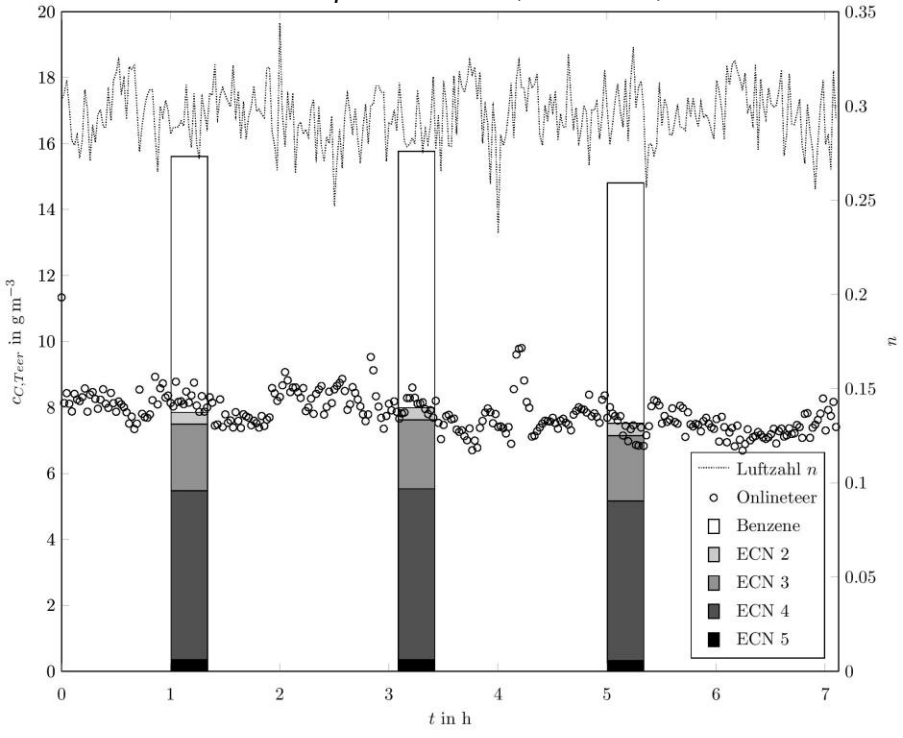


- Volume of sample loops 1 & 2 flushed to FID successively.
- Tar substances of sample loop 1 are condensed on a cooled “tar filter”.
- Measurable components (groups):
  - Total hydrocarbon
  - Non-condensable HC
  - “Tars” (condensable HC)

FID Online Total Tar Analyzer TTA300

Comparative measurements with „Tar Protocol“

Gasification of wood pellets: 800°C, air ratio 0,3



Validation of measurement principle:

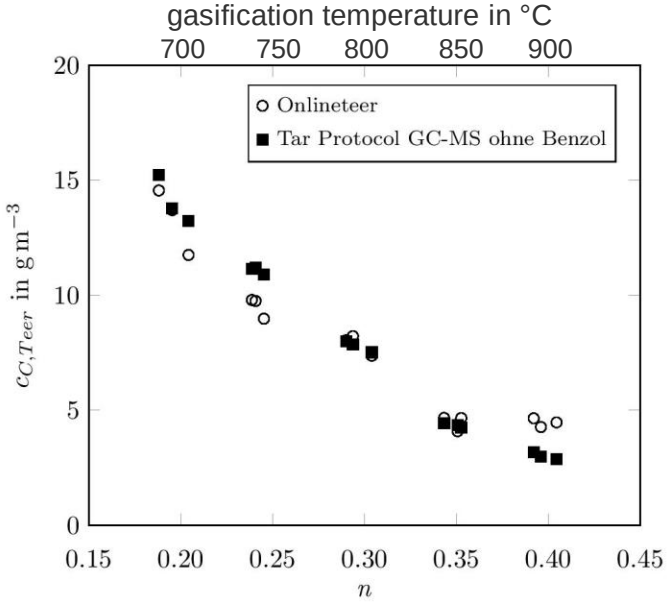
- Measurement cycle duration of 84 seconds corresponds to over 300 measurement cycles.
- Online measurements follow the wet chemical comparative measurements very clearly over total timeframe.
- Changes in tar concentrations by fluctuations in air ratio can be detected immediately.

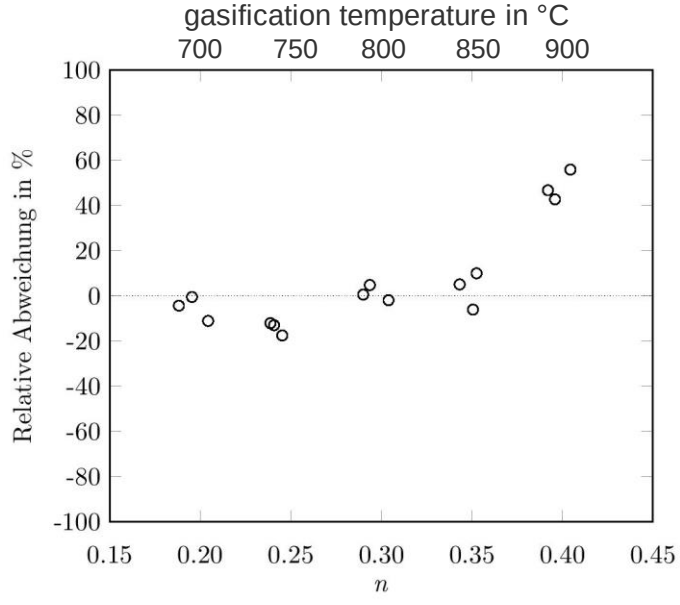
ECN Classification:
2: Heterocyclic HC (e.g. pyridine, phenol, cresol)
3: 1-ring HC (e.g. xylene, styrene toluene)
4: 2, 3-ring PAH (e.g. naphthalene, anthracene, phenanthrene)
5: > 3-Ring PAK (e.g. fluorathene, pyrene, chrysene

http://www.thersites.nl/classification.aspx

FID Online Total Tar Analyzer TTA300

Comparative measurements with „Tar Protocol“





- Absolute deviations in comparative measurements also in other gasifier operating conditions in a range of max. 1 g m^{-3}.
- At *low* tar concentrations (< 3 g m^{-3}) additional derivation is getting higher

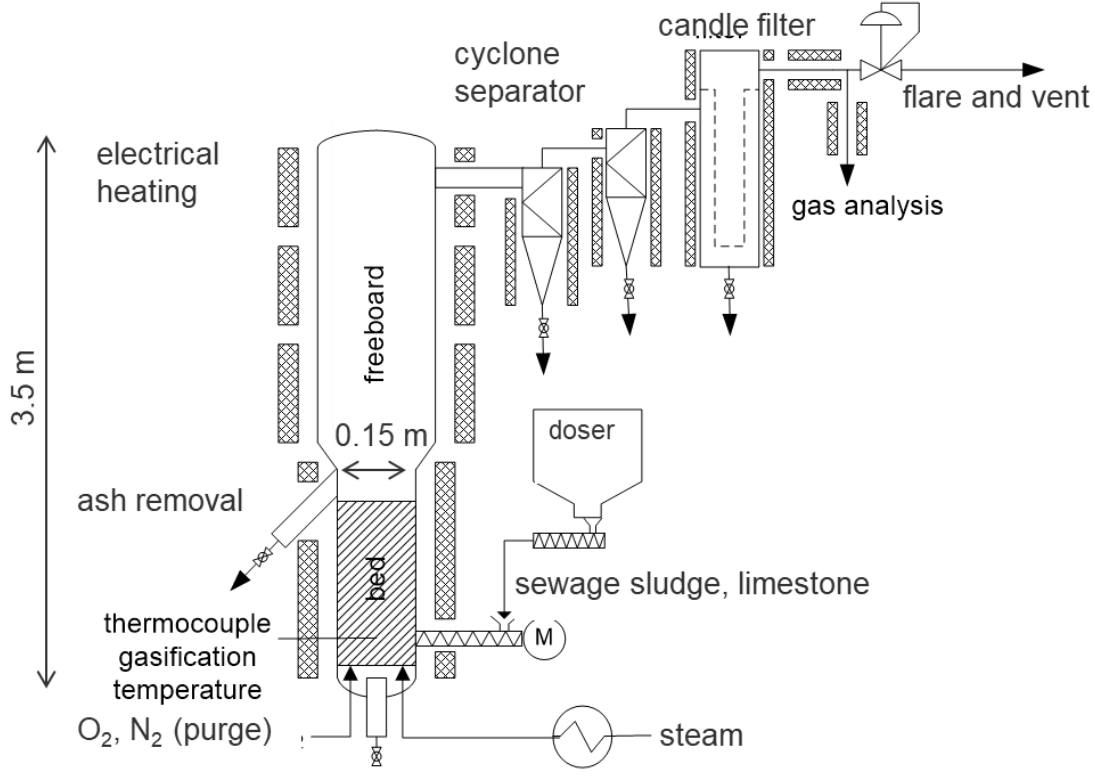
TTA 300 has good comparability to tar protocol and is an available device for raw gas monitoring

sulfur measurement at IFK

tar protocol at IFK

Sewage sludge gasification 20 kW gasifiaction tests

Tar and sulfur reduction with limestone as additive/sorbent

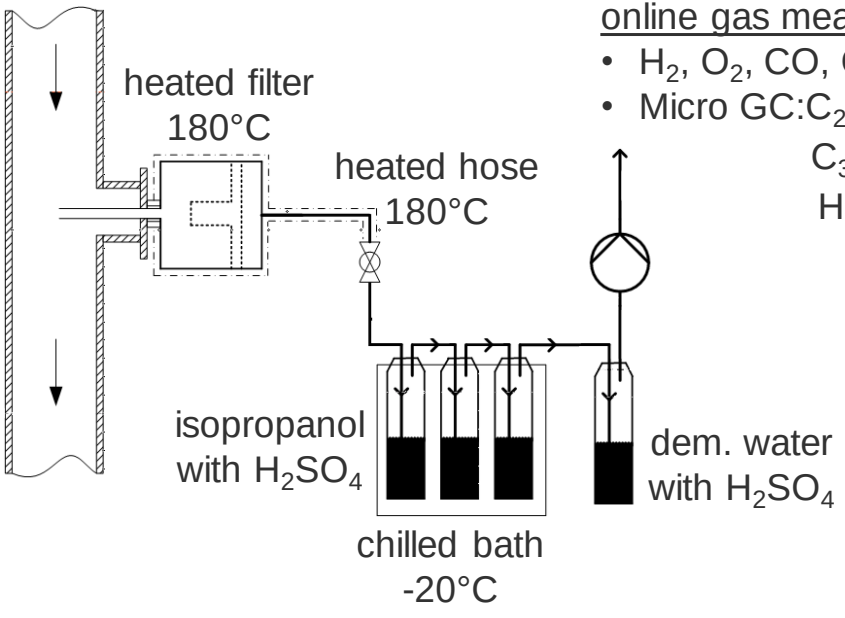


fuel: dried sewage sludge

analysis	in % kg/kg
H_2O	6.5
ash	47.6
C	51.0
H	6.9
O	32.0
N	7.5
S	2.4
Cl	0.2

Online gas measurement and sample gas preparation at IFK

Low cost H_2S and COS measurement via micro-GC

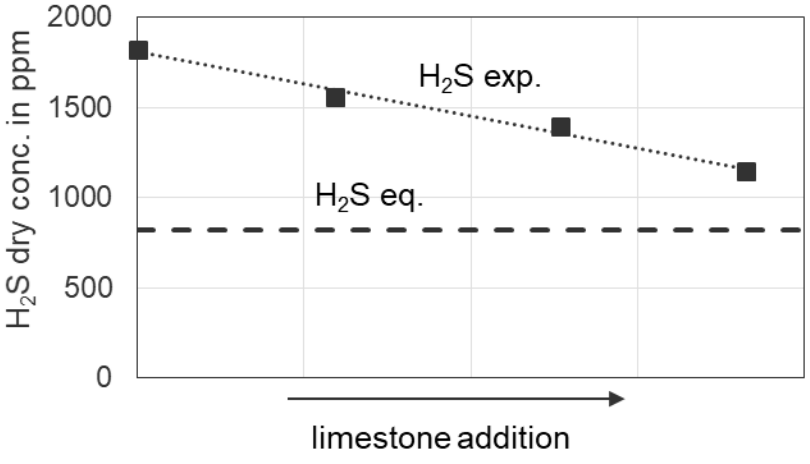


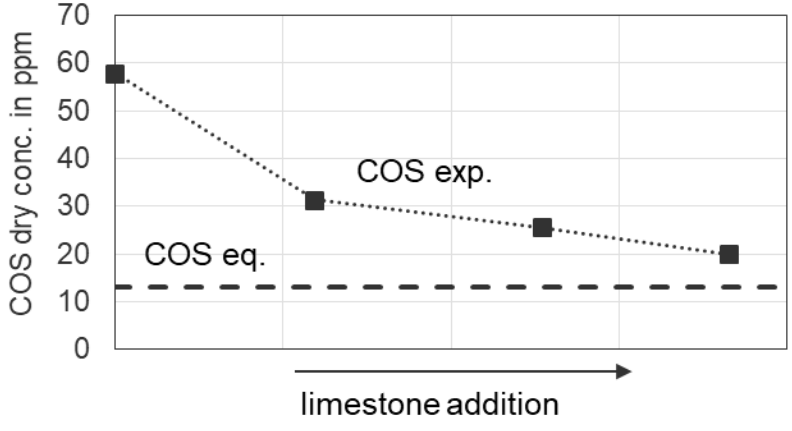
online gas measurement

- H_2, O_2, CO, CO_2, CH_4
- Micro GC: C_2H_4, C_2H_6, C_3H_6, C_3H_8 C_4H_{10} } C_xH_y
- H_2S, COS

- gas washing with isopropanol and water nesecessary to protect online gas analyzers
- sour washing liquid enables H_2S and COS to pass the gas washing bottles
- H_2S and COS can be measured down to ~5 ppm

Sulfur reduction with limestone as sorbent





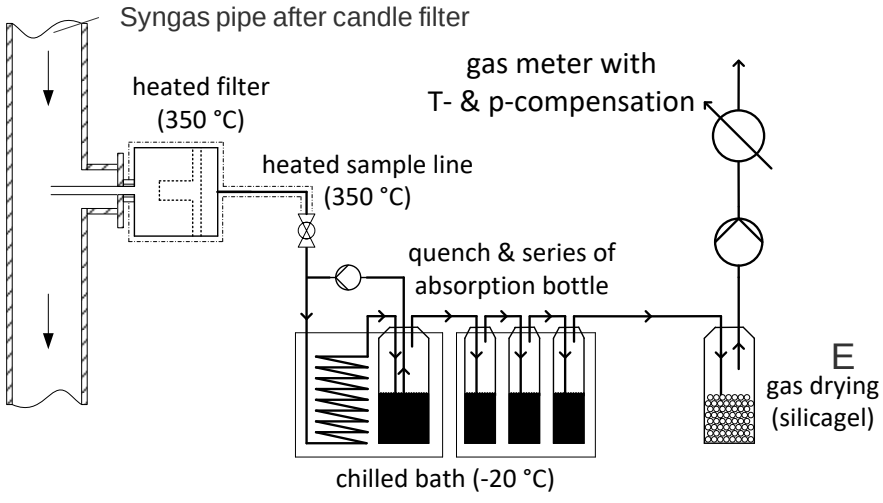
$CaO + H_2S \rightarrow CaS + H_2O$

$CaO + COS \rightarrow CaS + CO$

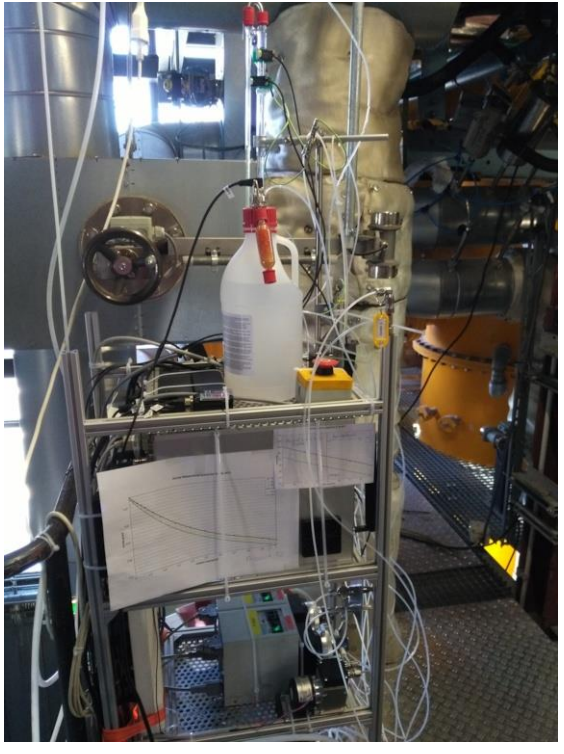
- higher limestone additive ratio reduces H_2S concentration
- H_2S concentration heads torwards equilibrium for high additive ratios
- micro-GC als reliable sulfur measurement device

Tar protocol – wet chemical sampling

IFK‘s wet chemical tar sampling system

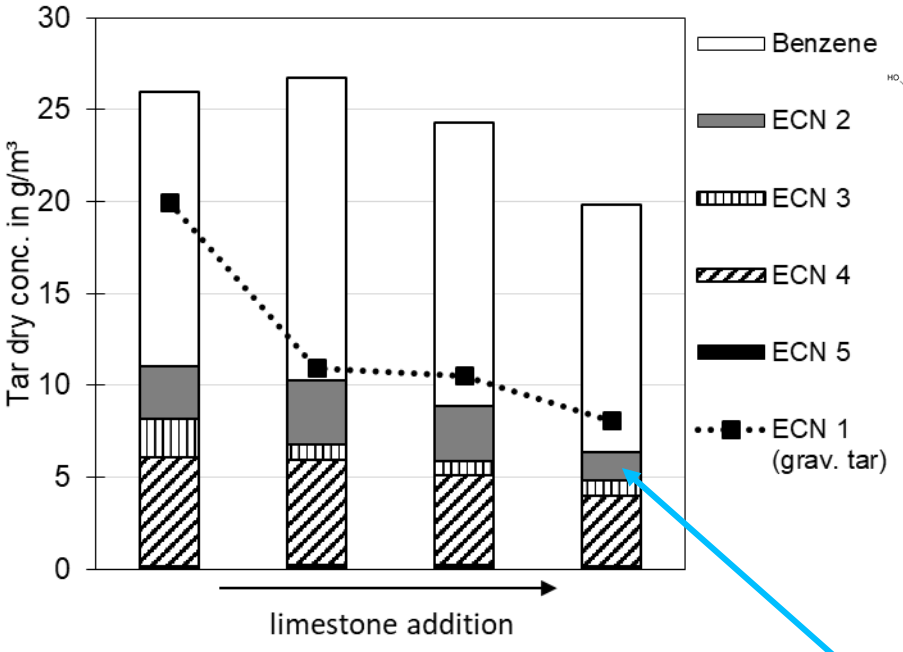


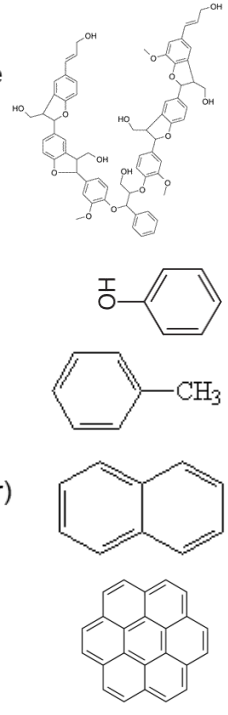
PSI‘s automatic liquid quench test at IFK‘s pilot plant



- Absorption liquid: Isopropanol
- Liquid is sampled and analysed
  - gravimetrically at IFK
  - GC-FID at FAU
  - GC-FID and GC-SCD at PSI → additional N and S-containing tars for residue gasification

Sar reduction with limestone as bed additive





tar classification

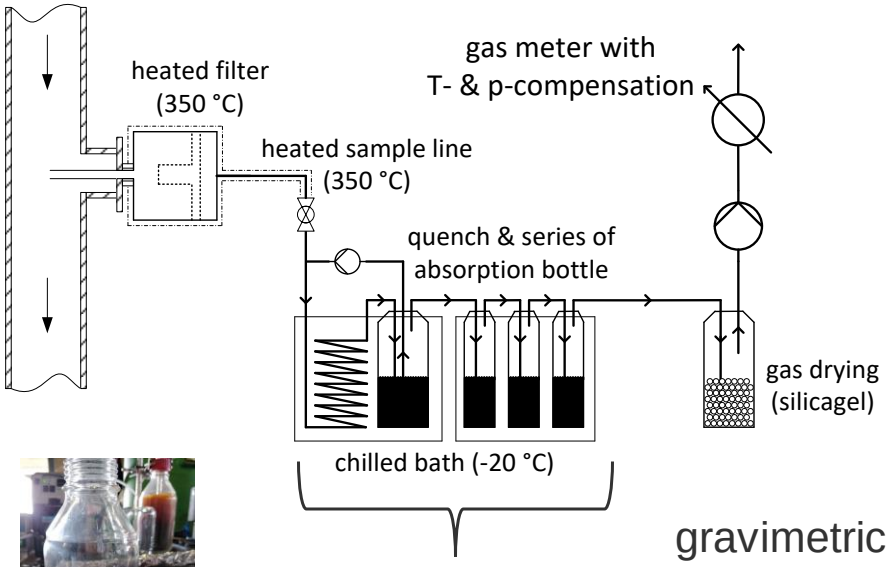
Class	anal.	description
ECN 1	gravim etric	gravimetric tars, condensable
ECN 2	GC-MS	water soluble tars
ECN 3	GC-MS	light aromatics, not condensable
ECN 4	GC-MS	light poly-aromatics (PAH), condensable
ECN 5	GC-MS	heavy PAHs, condensable

- substantial reduction of gravimetric tars
- higher limestone additive ratios needed for GC-MS tar reduction

- additional relevant components quantified by PSI with GC-FID/SCD:
  - pyridine, carbazole, dimethylhydantoin 

  - thiophene, benzothiophene 

Gravimetric tar composition for residue gasification



precipitation
in tar sample

sample collection
centrifugation

gravimetric
analysis

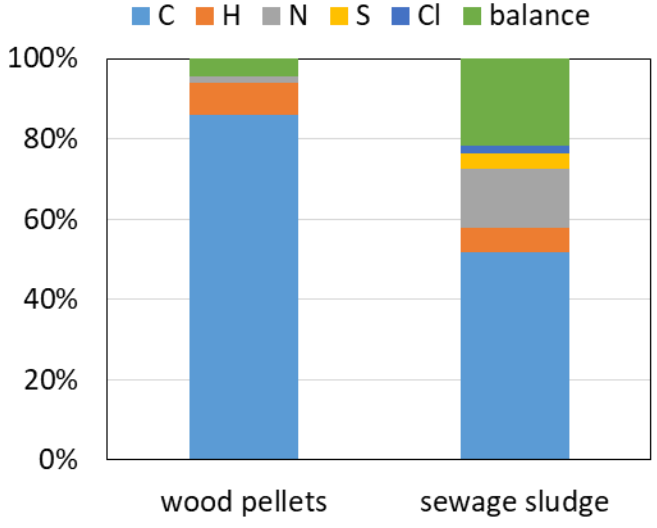
solid formation during gas sampling:

- ammoniumcarbonate:
  $2NH_3 + CO_2 + H_2O \rightarrow (NH4)_2CO_3$
- ammoniumchloride:
  $NH_3 + HCl \rightarrow NH_4Cl$

→ centrifugation removes most solids

→ some are detected as grav. tar

elemental analysis of gravimetric tars



planed online GC for gasification

Online-GC for gasification

planed acquisition at IFK

requirements:

- sample line temperature incl. valves min. temp. 250°C
- measurement time < 30 min
- measured components
  - BTX (→ biggest fraction of „tars“)
  - C_1-C_6
  - NH_3
  - HCl
  - H_2O
  - permanent gases

- online coupling to IFK‘s gasification rigs → instant data

Summary and conclusion

- TTA 300 has good comparability to tar protocol and is an available device for raw gas monitoring
- H_2S and COS measurement with mirco-GC is reliable for raw gas in residue gasification
- liquid sampling / tar protocol is still needed to characterize tars
  - for residue gasification additional GC detectable tar species need to be considered
  - solid formation needs to be considered for gravimetric analysis
  - endeavor to reduce liquid sampling effort by PSI's automatic liquid quench system
- new online GC planned at IFK

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Thank you!

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