Tar conversion over process char
Tar measurement with Petersen column and SPA method

Giulia Ravenni, PhD Student

DTU, CHEC Centre, Biomass Gasification Group

Supervisors:
Ulrik Birk Henriksen
Jesper Ahrenfeldt
Zsuzsa Sárossy
Benny Gøbel (DONG Energy)

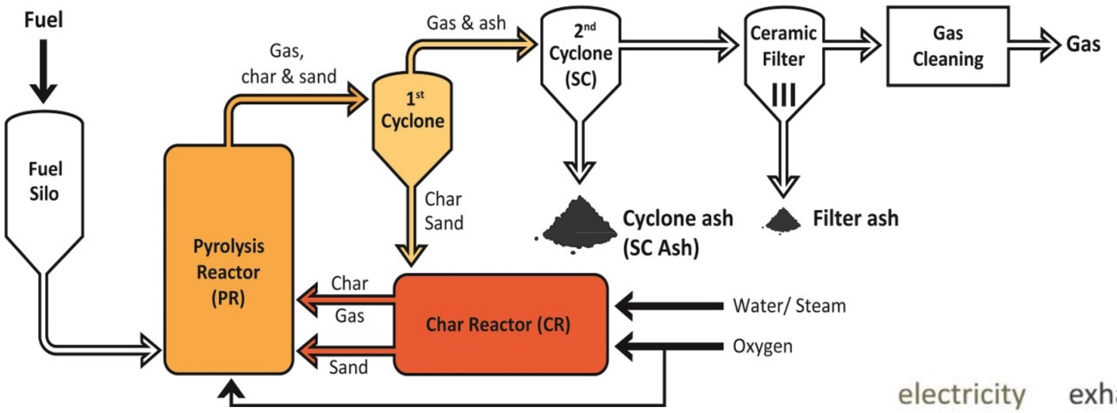
Gas Analysis Workshop

Berlin September 7th, 2017

Outline

- Viking and LT-CFB: double stage gasifiers at DTU, Risø
- Synfuel project and hot gas cleaning with process char
- Experimental setup at DTU for char bed testing
- Tar sampling and analysis techniques: a comparison between SPA and Petersen Column
- Overview of gas analysis activities at DTU, Biomass Gasification Group (BGG)

Double stage gasifiers at DTU, Risø

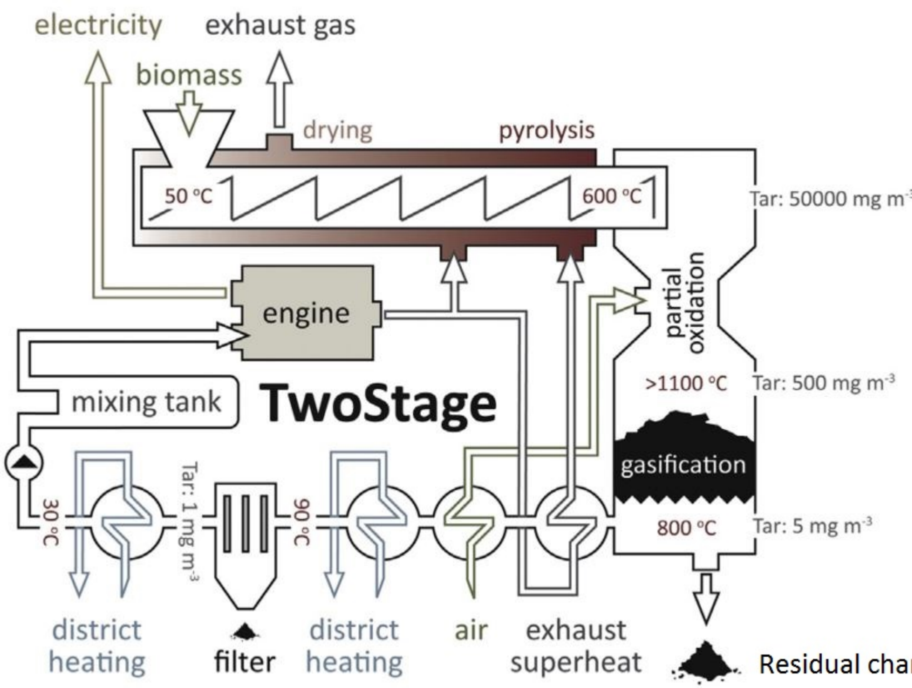


LT-CFB gasifier

- Fluid bed; max process temperature 750°C
- Suitable for low quality fuel (straw, sludge)
- High tar content in the producer gas

TwoStage gasifier (Viking)

- Almost tar-free gas
- Producer gas directly applicable to a gas engine fuel
- High quality biomass fuel required (wood chips)



Synfuel project – WP2: Improved gas cleaning

https://energiforskning.dk/en/node/8087

Project aim: find novel and viable solutions for producer gas cleaning (mainly from tars)

- Why the gas cleaning is so effective in the TwoStage process?
- What is the role of the fixed char bed in tar decomposition?
- Can this effect be replicated and applied to other gasification platforms?

BET surface area: 1030 m^2/g

Total pore volume: 0.75 cm^3/g

→ Physical and chemical **characterization** of the TwoStage residual char

→ Dedicated **laboratory setup** to investigate the interaction between a **bed of residual biochar** and tar model compounds **(phenol, naphthalene)**

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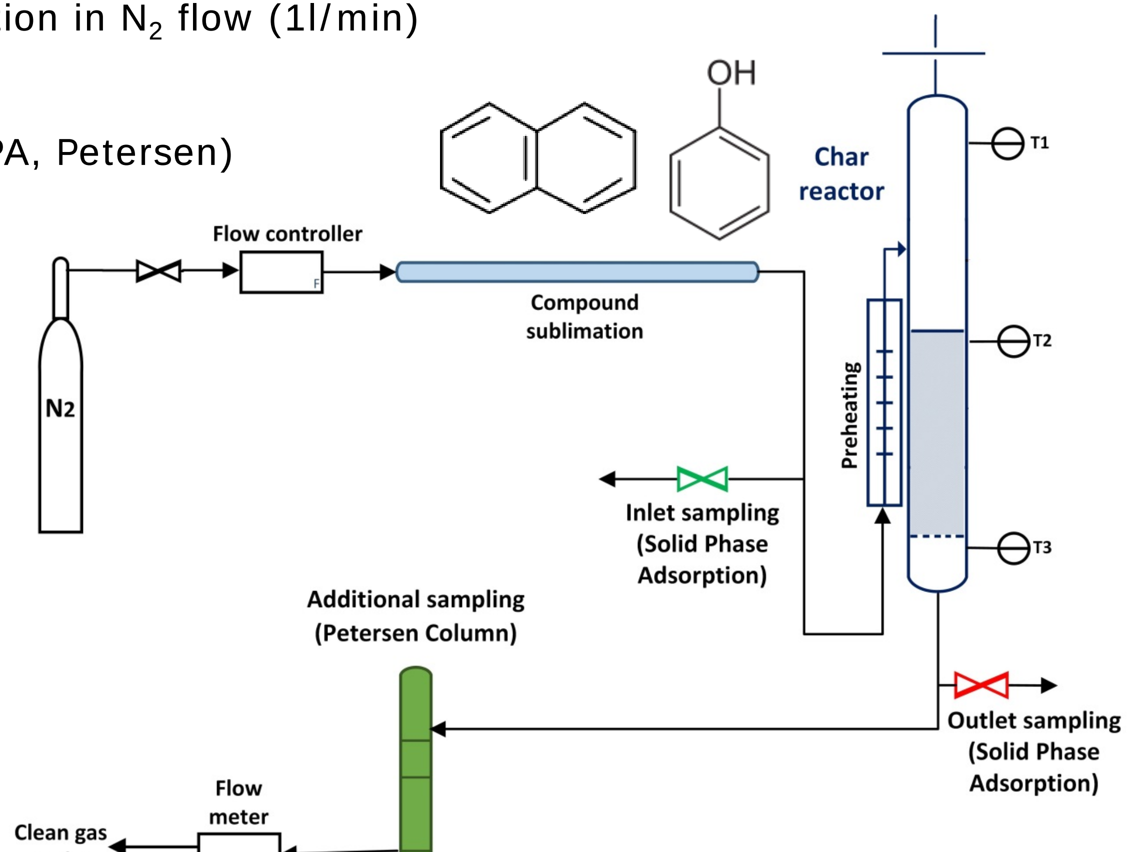
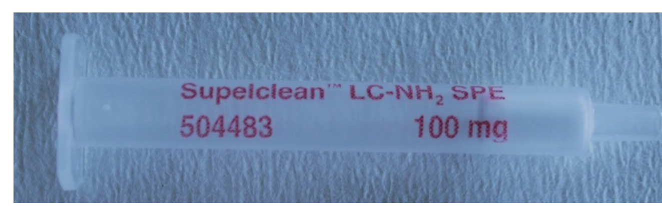
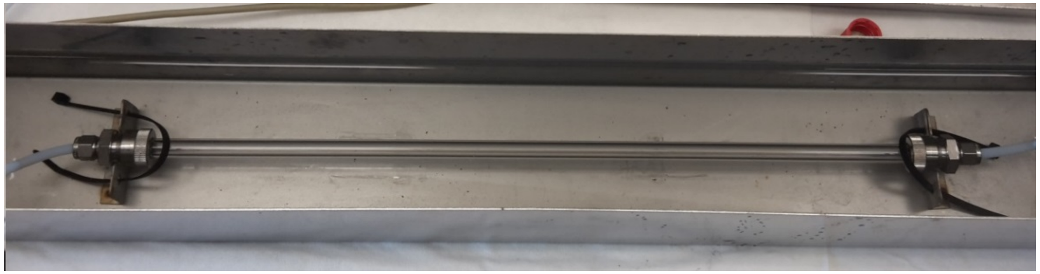
Experimental set up

- Phenol, naphthalene: sublimation in N_2 flow (1l/min)
- Contact with hot biochar bed
- Inlet - outlet gas sampling (SPA, Petersen)





Experimental set up



<u>60 minutes experiment</u>

- 3 SPA samples inlet (100-200ml gas)
- 3 SPA samples outlet
- 60 min Petersen at outlet (~250ml acetone)

Samples analysis - quantification

Petersen
Acetone sample

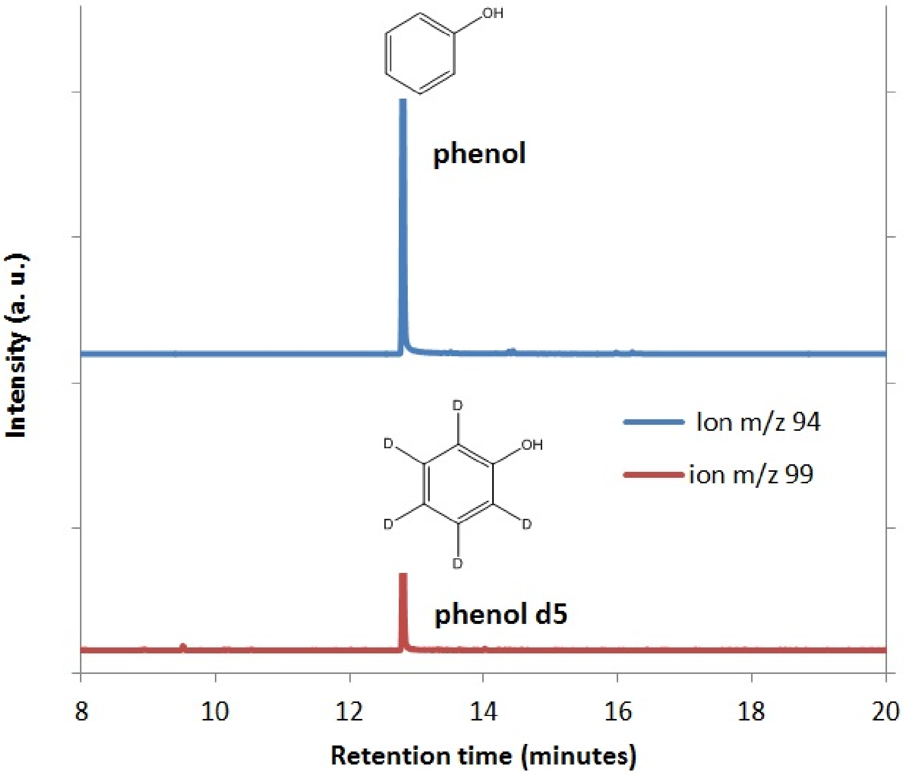
- Volume measurement
- Internal Standard added

SPA
Tubes

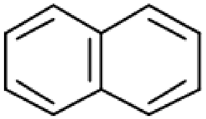
- Internal Standards added
- Overnight desorption

GC-MS analysis

→ Compound concentration [mg/m^3]



Results – Naphthalene

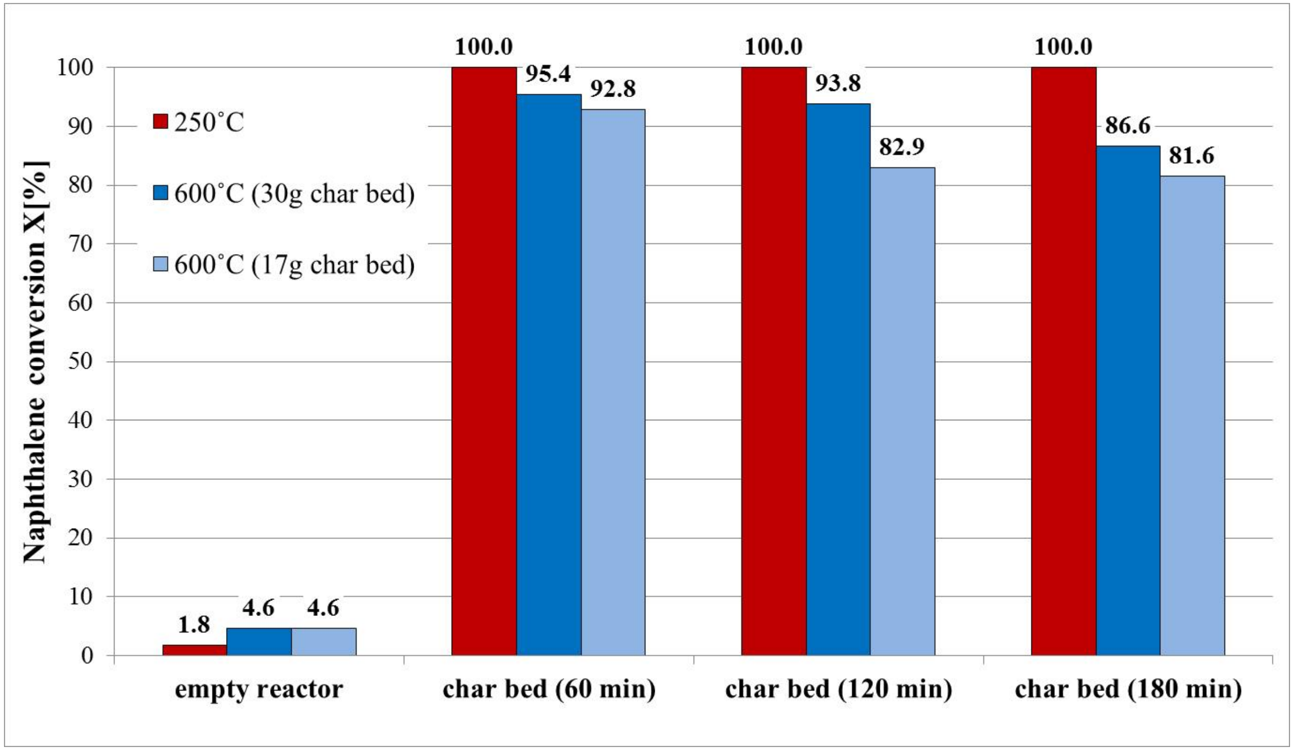


Experimental conditions:

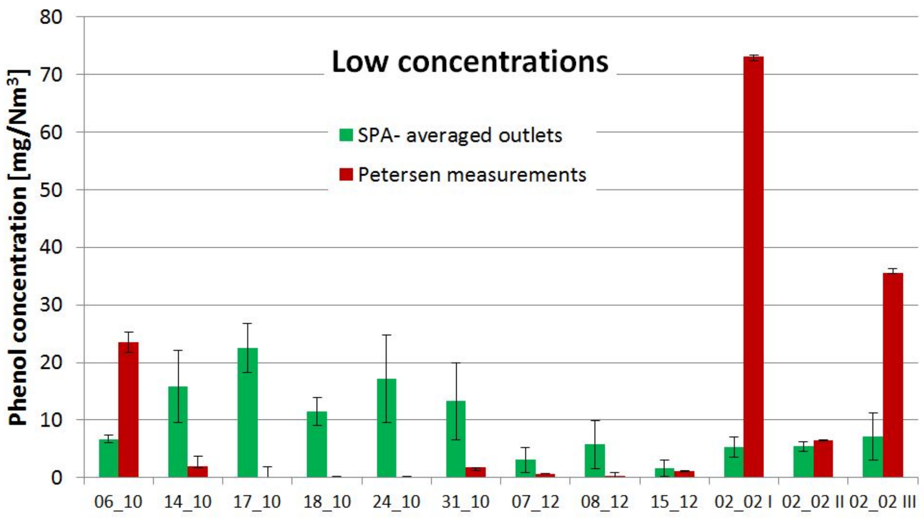
- Tested char bed temperatures: 250°C, 600°C
- Naphthalene concentration measured at inlet: C_{in} = 234 ±37 mg/Nm^3
- Reactor conditions: Empty reactor, char bed (30g and 17g)
- Residence time: 10.4s (250°C), and 6.2s (600°C) and 2.7s (600°C, 17g char bed)

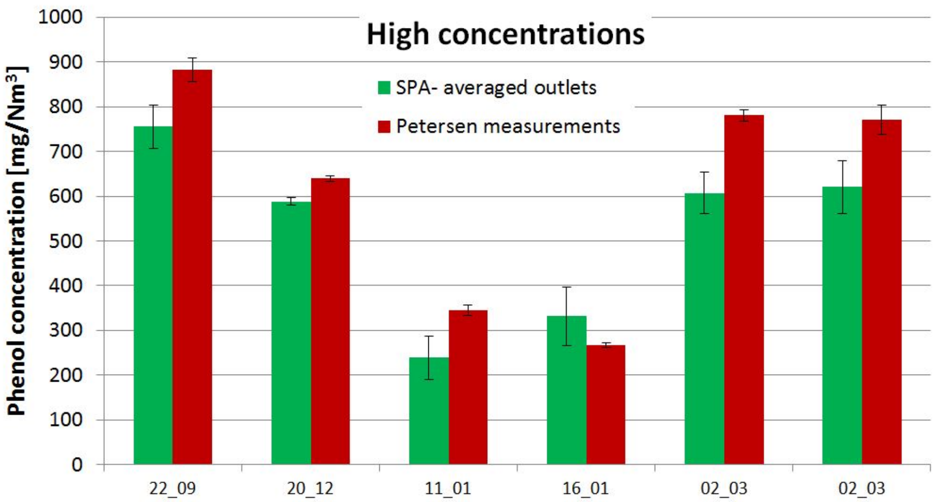
- Degree of conversion (X) calculated with SPA values

$$X = \frac{C_{in} - C_{out}}{C_{in}}$$

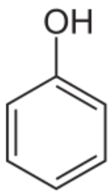


SPA –Petersen column comparison





Phenol



<u>Results comparison</u>

- Averaged 3 SPA samples over 1 hour
- 1 hour Petersen sampling

Low concentration

- High discrepancy and high deviation of results

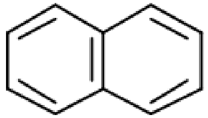
High concentration

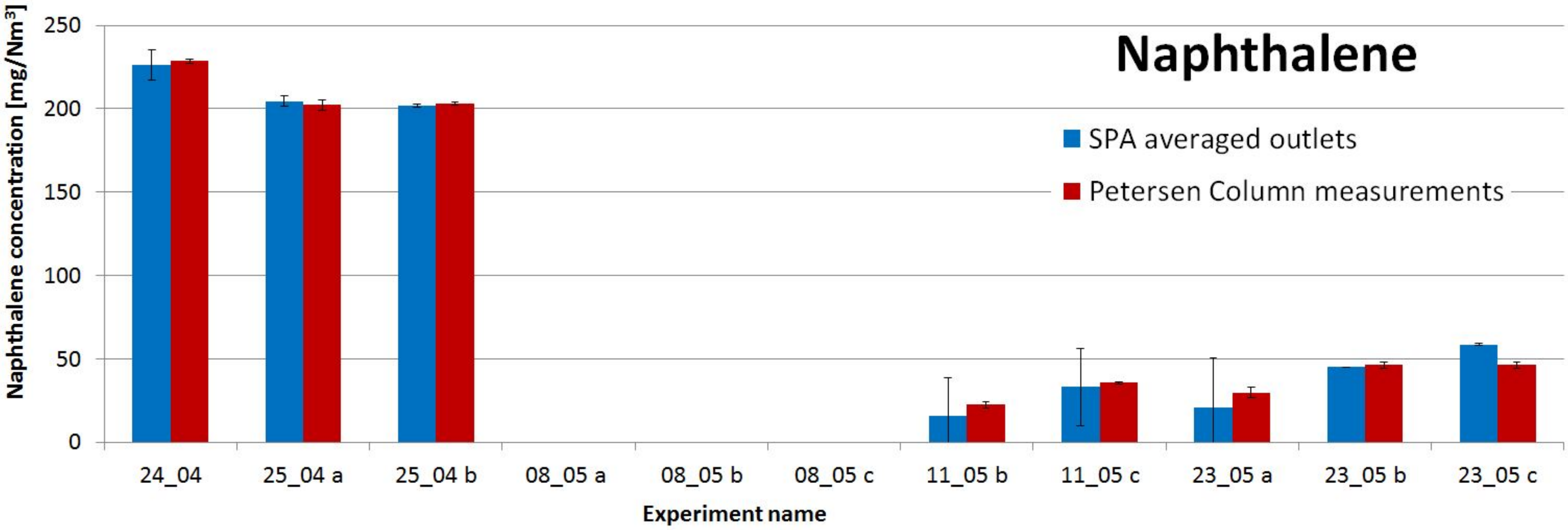
- Lower deviation and increased agreement between SPA and Petersen

SPA –Petersen column comparison

Naphthalene: results comparison

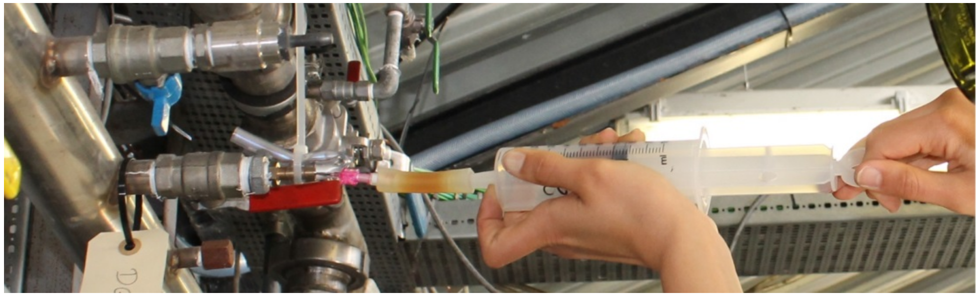
- Averaged 3 SPA samples over 1 hour
- 1 hour Petersen sampling

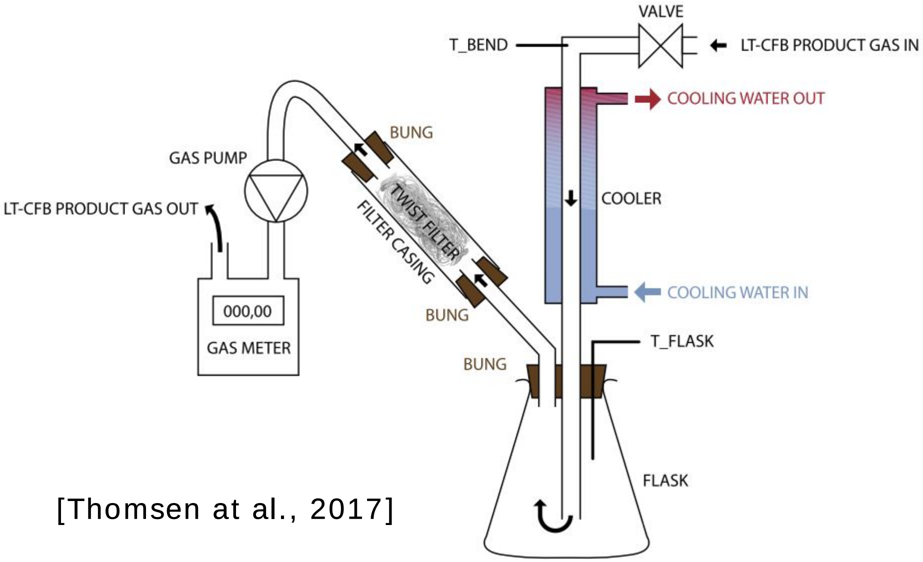




Gas analysis activities at DTU

- Tar sampling **SPA** and **Petersen Column** + internal standard- GC-MS quantification (phenol, naphthalene, PAHs)
- Quantification of **gravimetric tar** and **water content** in producer gas for energy and mass balance





[Thomsen at al., 2017]

Gas analysis activities at DTU

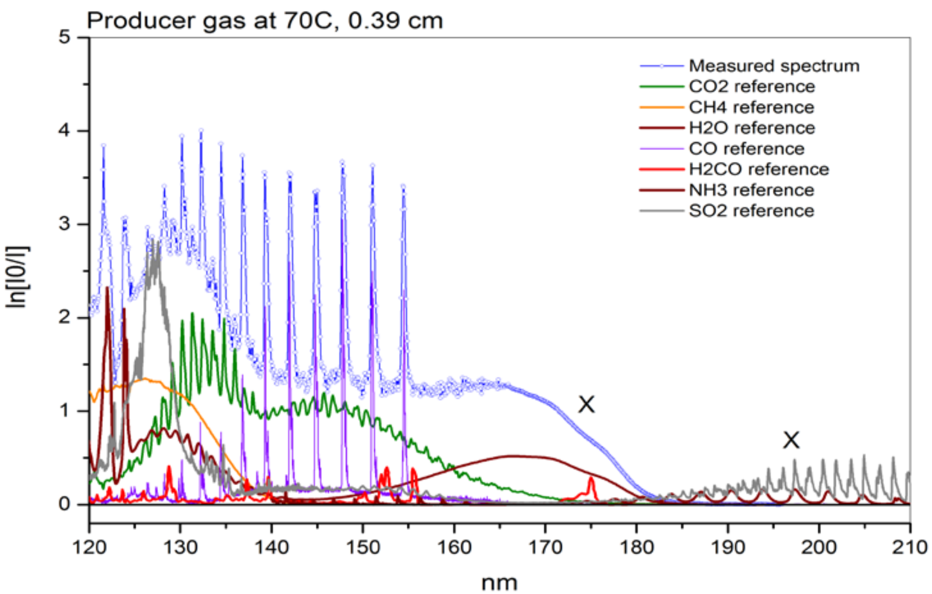
- Gas analyzer (online)
- Gas pipettes sampling for permanent gases + GC-TCD analysis (offline)

In situ/on-line measurements

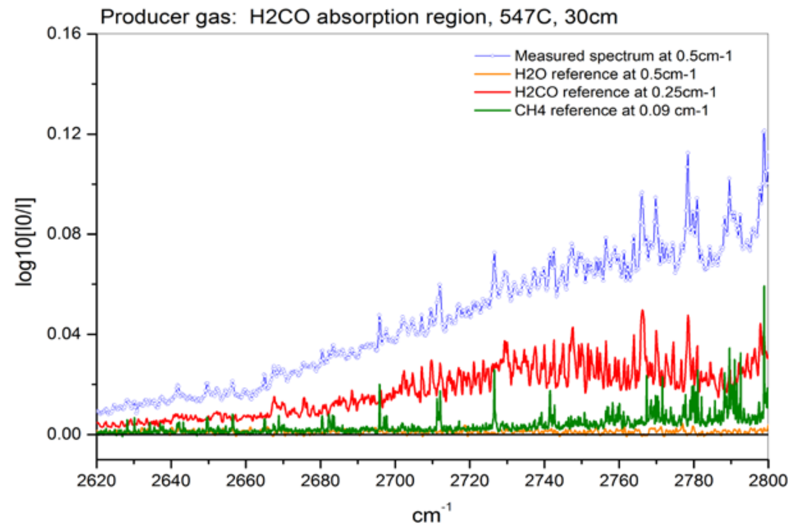
Contact: Alexander Fateev: alfa@kt.dtu.dk

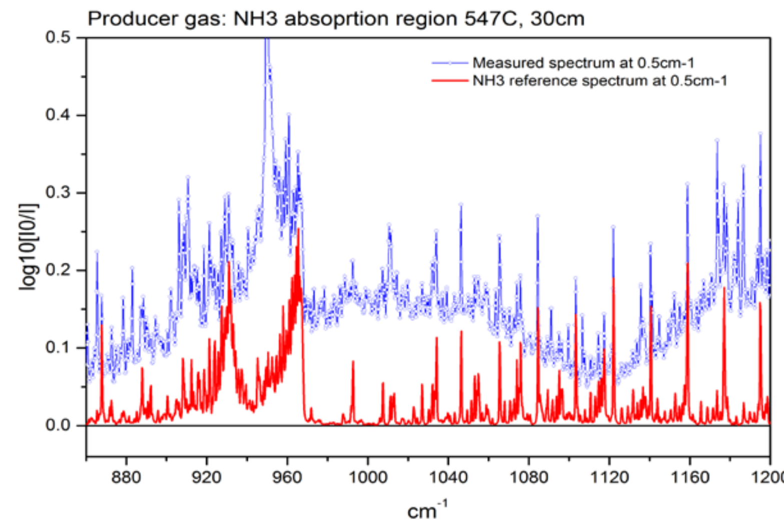
- FTIR (400-8000 cm^{-1}): 0.25..0.5 cm^{-1};
- (Far) UV (160-400 nm) absorption spectroscopy;
- In situ: directly over 0.004 m to 4 m
- On-line gas extraction (150 ˚C)
- On-line by bypass at T_gas <= 300ºC
- Measurements at different levels of concentrations

On-line far UV absorption spectrum (Viking gasifier)

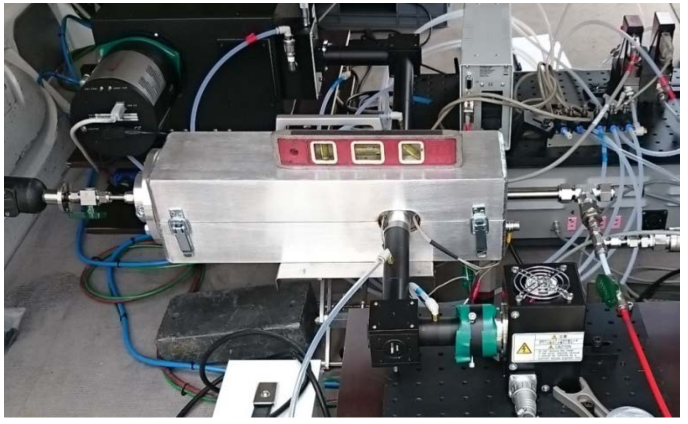


In-situ FTIR absorption spectrum (LT-CFB)

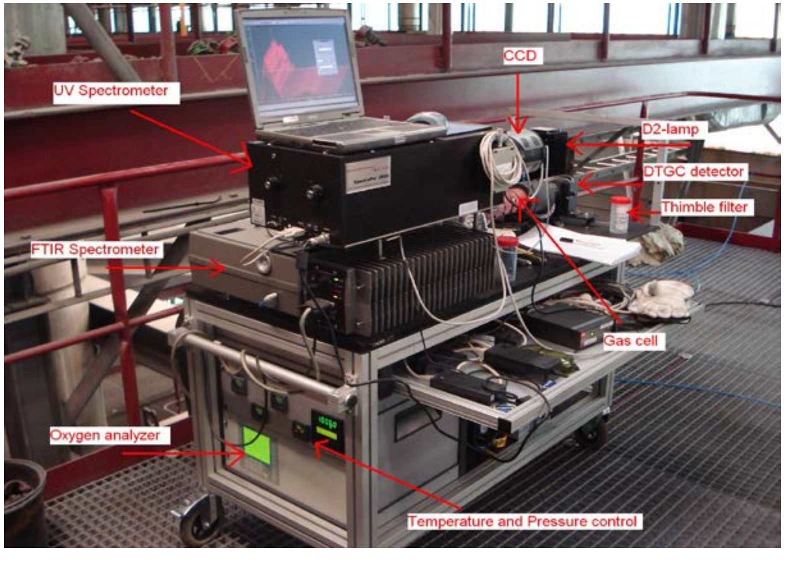




Equipment implementation examples

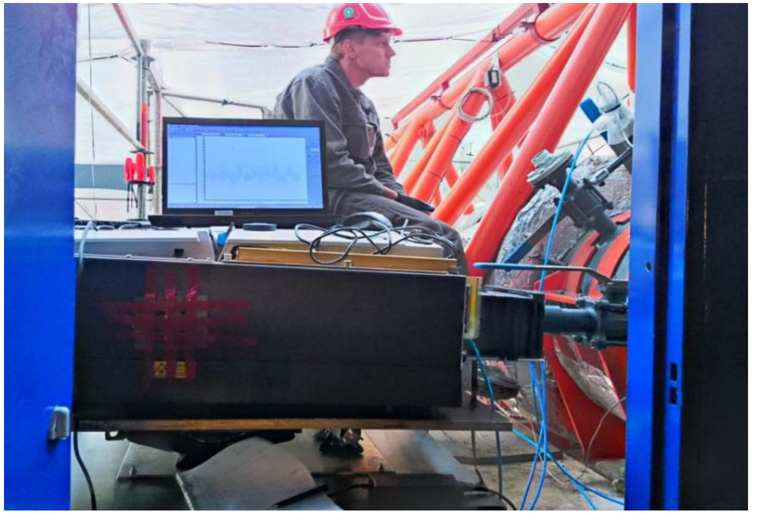


Gas cell for far UV absorption measurements up to 300 °C



Gas extraction system for simultaneous UV/IR/O_2 measurements at 150 °C

FTIR absorption measurements on the LT-CFB Pyroneer gasifier (Kalundborg, DK)



Thank you for your attention ☺

Questions?

References

Tar measurements on Viking and LT-CFB gasifiers

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- [2] Ahrenfeldt J, Henriksen U, Jensen TK, Gøbel B, Wiese L, Kather A, et al. Validation of a continuous combined heat and power (CHP) operation of a two-stage biomass gasifier. Energy and Fuels 2006;20:2672–80. doi:10.1021/ef0503616.
- [3] Ahrenfeldt J, Egsgaard H, Stelte W, Thomsen T, Henriksen UB. The influence of partial oxidation mechanisms on tar destruction in TwoStage biomass gasification. Fuel 2013;112:662–80. doi:10.1016/j.fuel.2012.09.048.

Spectroscopy applied to gasification

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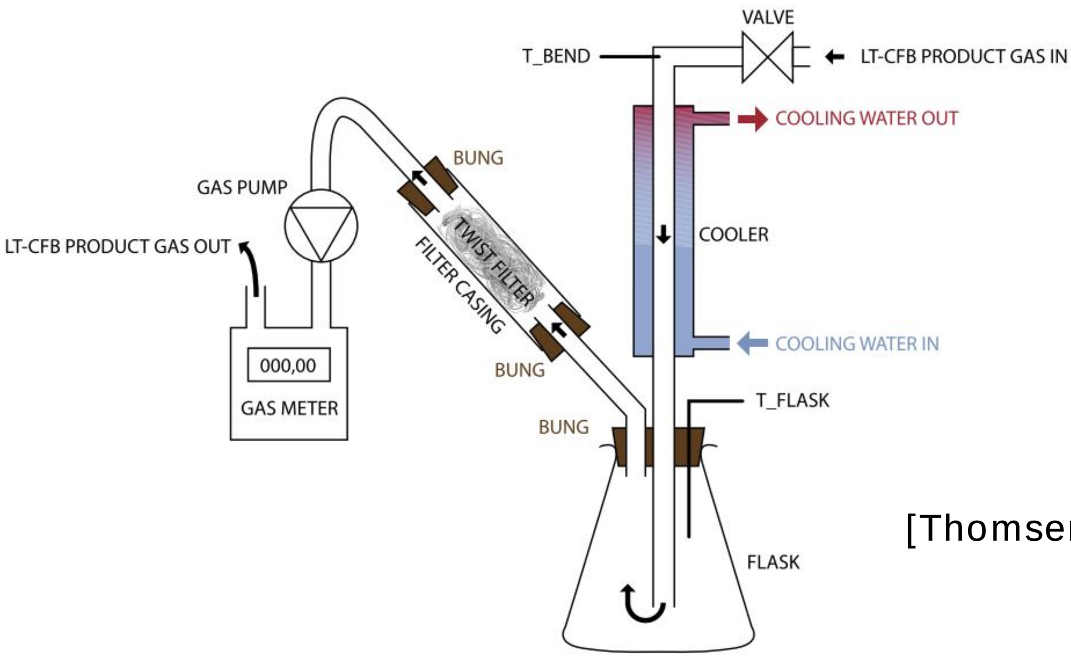
- [5] Grosch H, Sárossy Z, Egsgaard H, Fateev A. UV absorption cross-sections of phenol and naphthalene at temperatures up to 500C. J Quant Spectrosc Radiat Transf 2015;156:17–23. doi:10.1016/j.jqsrt.2015.01.021.

Gas analysis activities at DTU

Quantification of gravimetric tar and water content in producer gas

- Condensate from producer gas is collected in the flask in two fractions: with and without water
- Total volume of sampled gas is measured with gas meter
- Calorimetry tests are run on water and water-free phases. Assuming the heating value of gravimetric tar, the amount of water in the gas is derived



[Thomsen at al., 2017]

Gas analysis activities at DTU

Chromatography equipment

- Agilent GC HP6890 coupled with Agilent MS 5973
  Column:WCOT-fused silica column
- Agilent GC 7890A with FID detector
  Columns: Porapak , Molecular Sieve 5Å

Synfuel project