Tar analysis methods for small scale gasification systems

…from a KTH perspective…

Klas Engvall

KTH Royal Institute of Technology

Dept. of Chemical Engineering and Technology

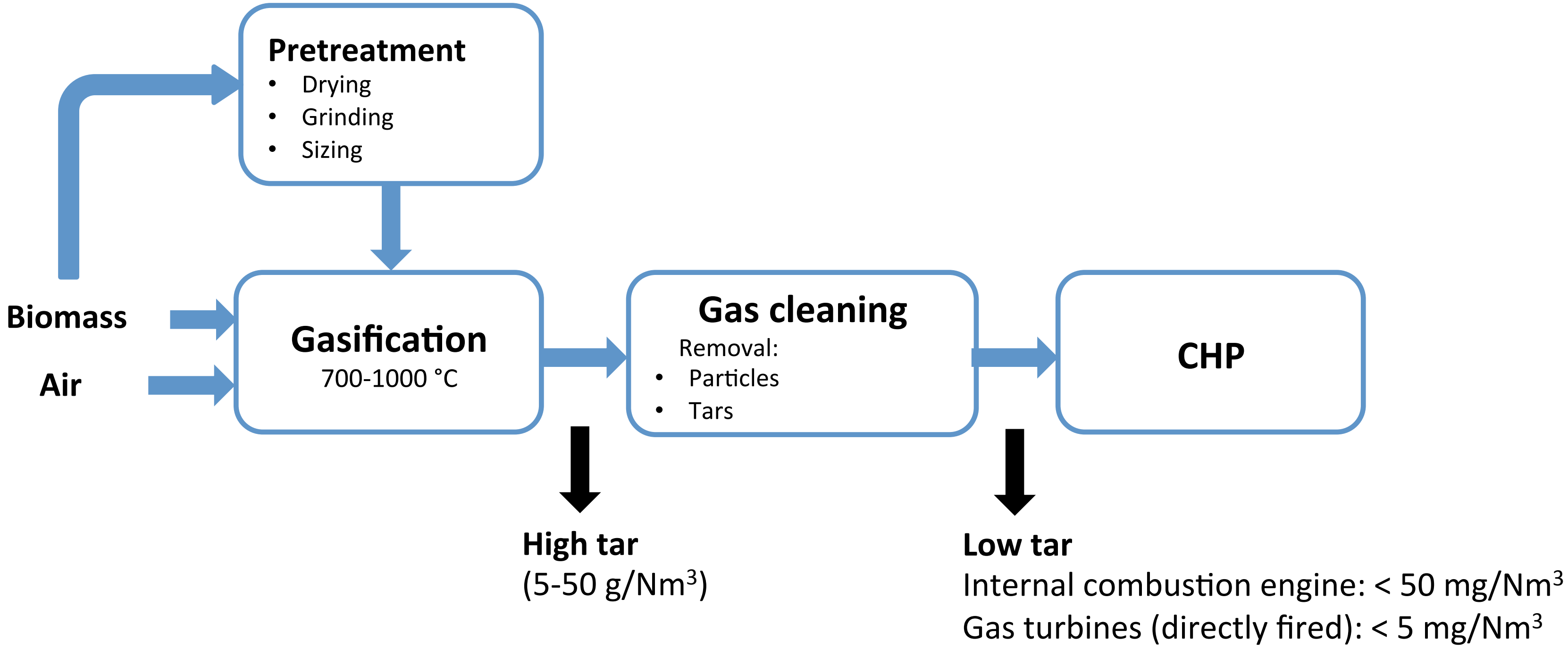
Stockholm, Sweden

Outline

- Background
- Tar analysis in a small scale gasification system
  - Offline methods
    - "Conventional" tar analysis
    - Solid Phase Absorption (SPA)
    - SPME
  - Online methods
    - FID
    - PID
  - What is the conclusion?
- Summary

Background

Small scale gasification systems

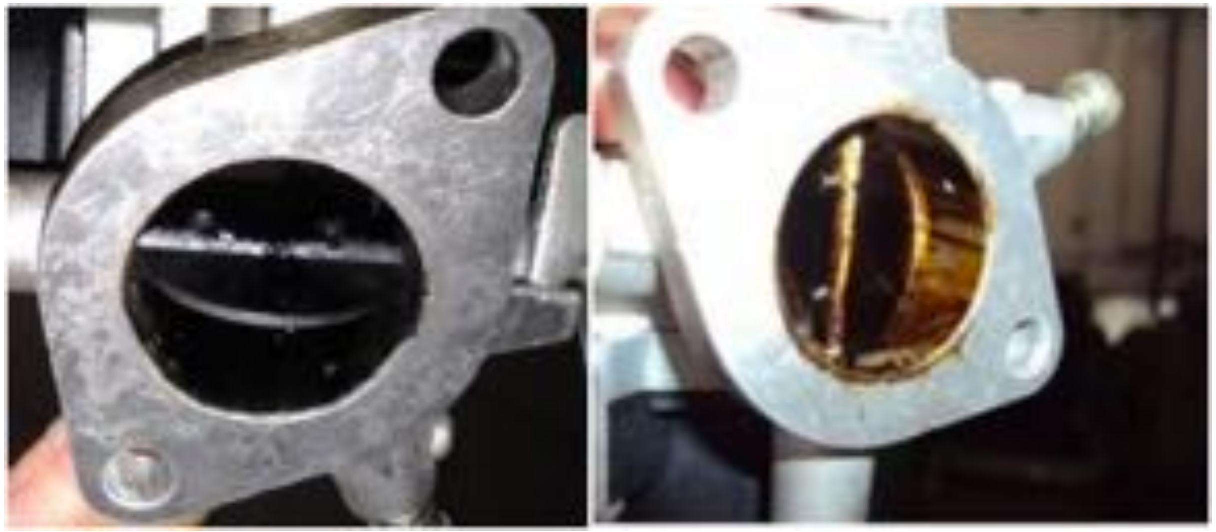


Challenge biomass gasification tars

- Production of condensable polyaromatic “tars” is inherent in most biomass gasification processes
- Tars foul and can plug equipment downstream of the gasifier
- Challenging to remove from the produced gas
- Reduce energy efficiency of gasification process
- Reports of as much as 10 % of biomass carbon ending up in the form of tars

Challenge biomass gasification tars

Example internal combustion engine



Throttle valve tar deposits with water scrubbing (left) , oil scrubbing (right)

N. Moriconia, et al., Design and preliminary operation of a gasification plant for micro-CHP with internal combustion engine and SOFC. Energy Procedia 81 (2015) 298 – 308

What is tar?

The term "tar" is vague and the definition vary.

One definition is "organic molecules with a molecular weight higher than that of benzene” (Mw = 78 g/mol).

What is tar?

Light tars

Organic compounds that can be analysed with GC as well as HPLC. (Mw 79-300 g/mol). They are **volatile and semi-volatile aromatics and phenolics**.

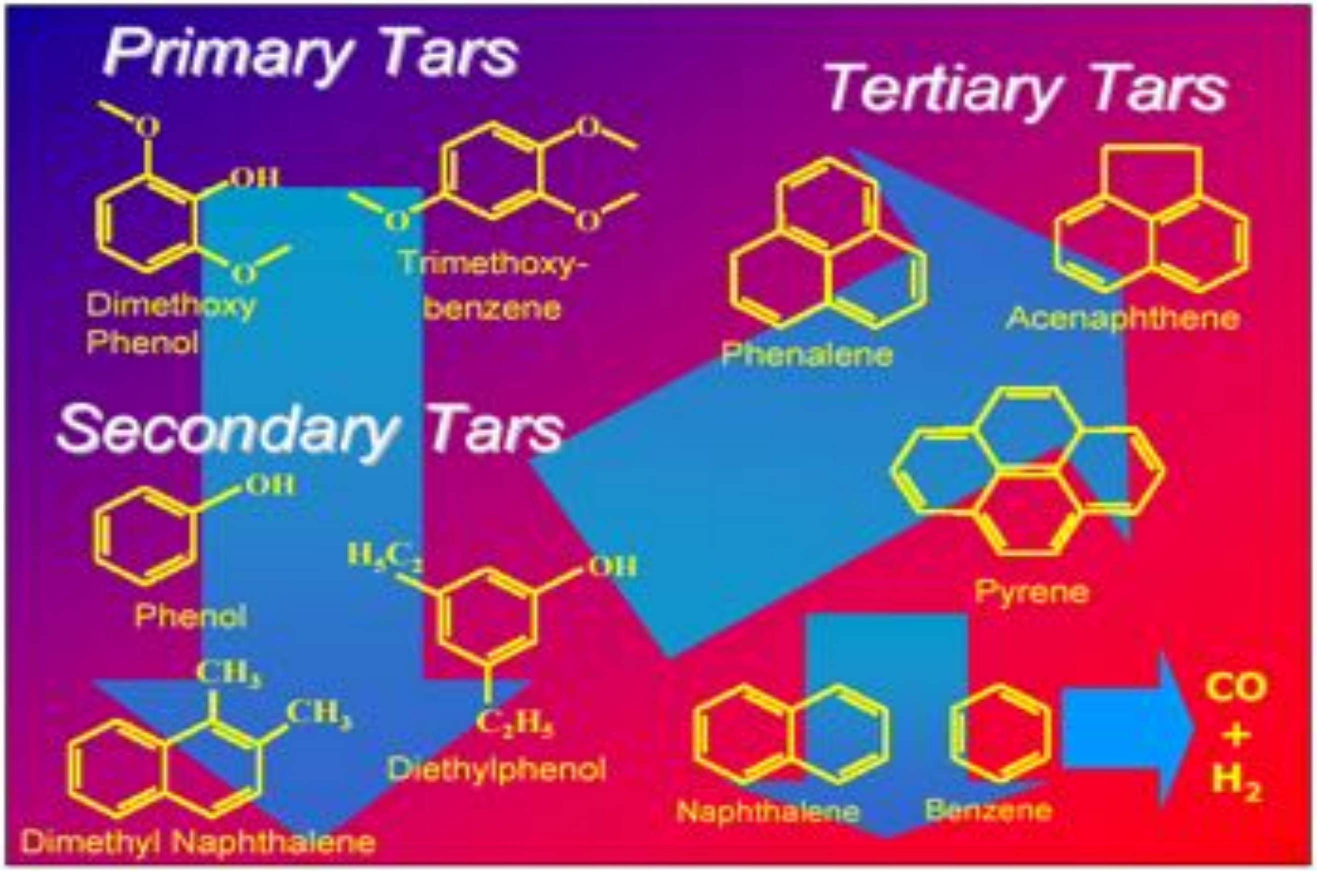
Heavy tar

Organic compounds with so high boiling points that they can be analysed only by HPLC, not with GC. **They are mixtures of high molecular weight ”non-volatile” polar compounds (Mw ≈>300 g/mol)**

Total tar = sum of light and heavy tar

What is tar?

Oxygenated compounds



Polycyclic aromatic compounds

Phenolic compounds and olefins

General scheme tar analysis

A few common steps:

1. Sampling of the tar: Generally collected from a side stream, including more or less complicated sampling equipment to attain a representative sample.
2. Storage of sample: Only valid for offline methods.
3. Pre-preparation/conditioning of the sample:

   Offline methods: The collected tars are extracted to or dissolved in an appropriate solvent for further chemical analysis.

   Online measurements: Conditioning such as drying of gas removal of particulates etc. may be required depending on the analytical technique.
4. Analysis of sample: Chemical analysis of pre-prepared/conditioned tar sample. Most common analytical techniques are based on gas chromatography (GC) or high pressure liquid chromatography (HPLC).

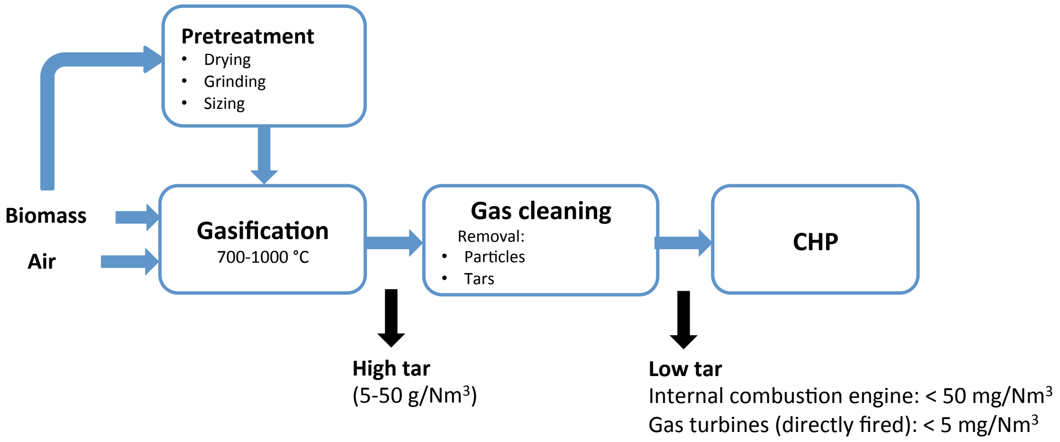
All these methods!

Method	Development status	Application	Measured data	Offline/ Online	Sampling and analysis time	Cost
Tar protocol/ guideline	CEN/TS pre-standard	Laboratory use	Gravimetric tar (Class 1) GC-FID (Class 2-5)	Offline	Long sampling and analysis time	Very expensive
Petersen column	Portable device	Laboratory use	Gravimetric tar (Class 1-5)	Offline	Long sampling and analysis time	Low
GC-FID and GC-MS	Not easy to transport	Laboratory use	Individual tar compounds (Class 2-5)	Offline/ Online	Short sampling time and relatively short analysis time	Expensive
HPLC	Not easy to transport	Laboratory use	Individual tar compounds (Class 1-5)	Offline/ Online	Long sampling and analysis time	Expensive
SPA	Easy to use probe	Laboratory use	Individual tar compounds (Class 2-5)	Offline	Relatively short sampling and long analysis time	Expensive
SPME	Easy to use probe. Under development	Laboratory use	Individual tar compounds (Class 2-5)	Offline	Relatively short sampling and long analysis time	Low
Online tar analyser]	Portable device	Industrial use	Individual tar compounds (Class 2-5)	Online	Relatively short sampling and analysis time	Expensive
MBMS	Transportable	Industrial use	Individual tar compounds (Class 2-5)	Online	Short sampling and analysis time	Very expensive
GC/LAMS	Transportable	Laboratory use	Individual tar compounds (Class 2-5)	Online	Short sampling time and relatively short analysis time	Very expensive
PID	Under development	Industrial use	Individual tar compounds (Class 2-5)	Online	Short sampling and analysis time	Low
Raman spectroscopy	Not transportable	Industrial use	Gravimetric tar (Class 1-5)	Online	Short sampling and analysis time	Very expensive

- Large number of methods for tar measurement
- Generally:
  - For research and laboratory use
  - Complex – needs expertize
  - Several are expensive
  - Not robust enough process
  - …

What method to use?

- Depends on information desired!
  - Qualitative or quantitative information?
  - Information about chemical composition?
  - R&D or industrial monitoring?
- Reliability?
- Costs?
- …



Requirements tar analysis small scale systems

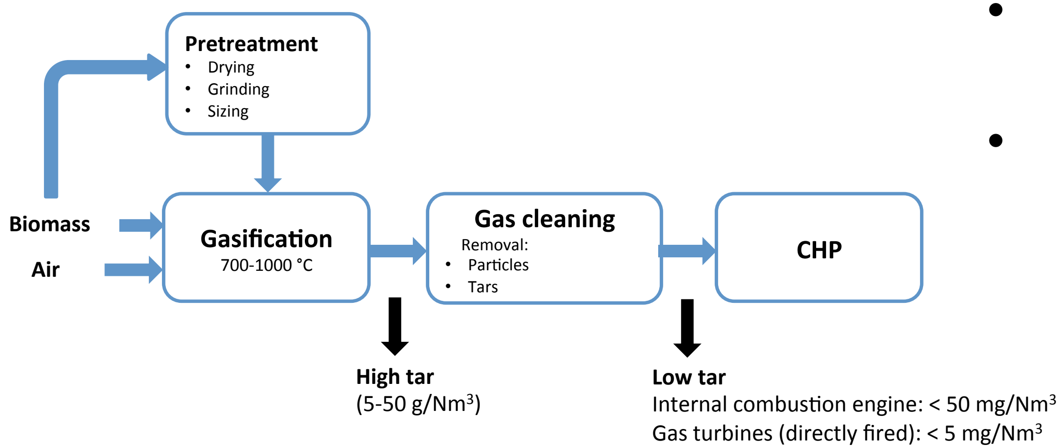
Research

No real requirements

“A matter of need to know and costs!”

Industrial monitoring/analysis

- Reliable - high repeatability
- Low staffing
- No or low need for expertise
- Low costs
- Fast
- Tar composition generally not of interest
- Preferably online



Tar analysis in a small scale gasification system

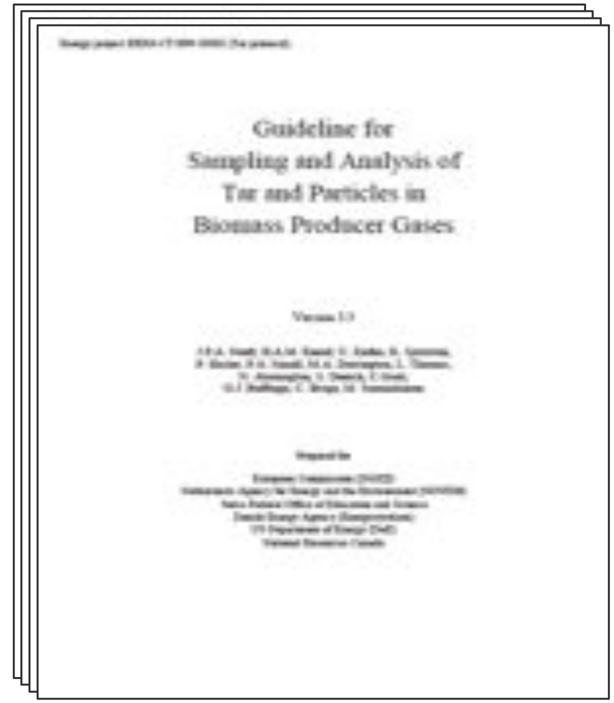
Offline methods

"Conventional" tar analysis

Tar protocol developed over several projects supported by IEA Bioenergy Task 33, US DOE and European Commission 1998-2005

- Significant contributions by ECN, VTT, KTH, DTI, BTG, NREL

Adopted as CEN standard for tar sampling


Guideline for
Sampling and Analysis of
Tar and Particles in
Biomass Producer Gases

CSN P CEN/TS 15439 - Biomass gasification - Tar and particles in product gases - Sampling and analysis (2006).

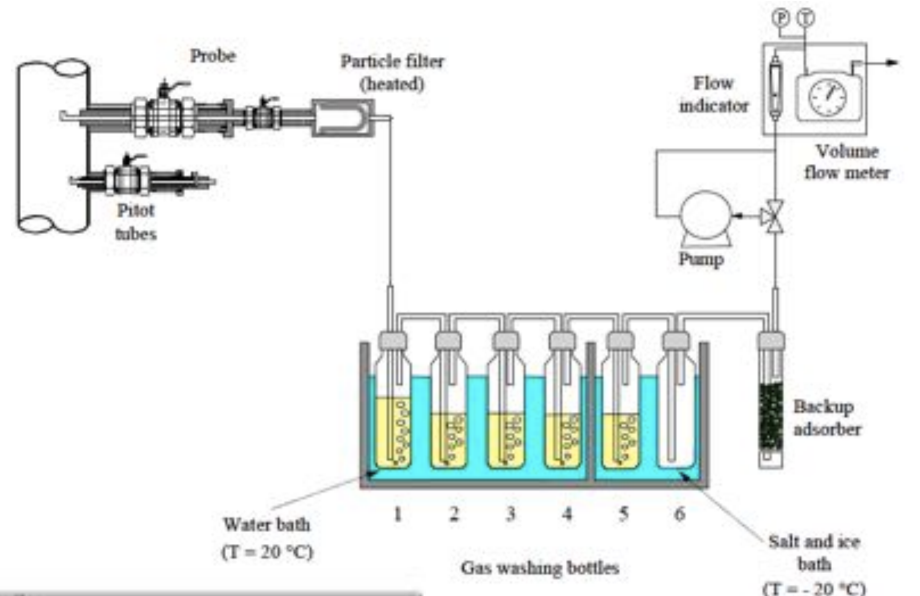
Offline methods

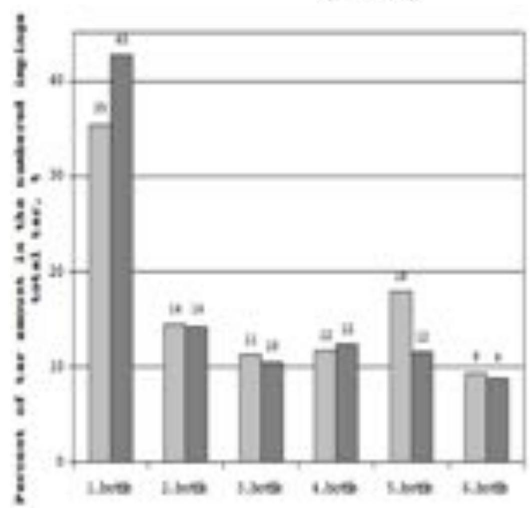
“Conventional” tar analysis

Procedure

- Draw specific volume of process gas through a filter and then a series of cold impingers to collect the tars
- Evaporate solvent to measure **gravimetric** (total) tars
- Analyze tars by **GC-MS to evaluate composition**

Quantitative, but very laborious





Offline methods

Solid Phase Adsorption (SPA)

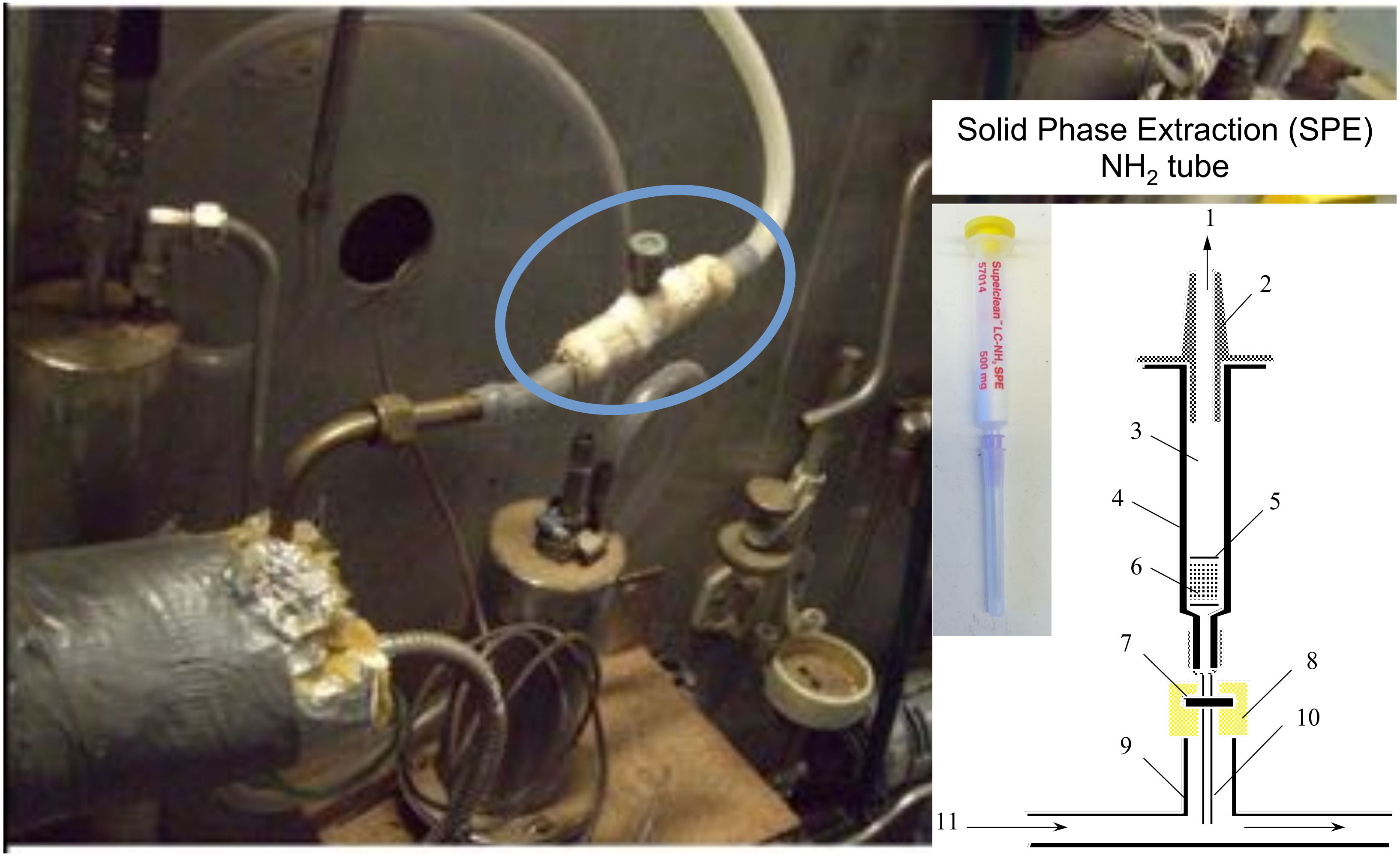
- SPA sampling and analysis method was developed by KTH in the 1990's.
- SPA used for measurement of the concentration (mass) of individual light aromatic hydrocarbons and phenols.
- The SPA-method is restricted to GC-available (GA) compounds only.
- These compounds are, however, significant process markers that provide good measures of reactor performance and gas quality.
- At T = 900°C and above the GA-compounds roughly correspond to the total tar amount.


Use of amino phase adsorbent for biomass tar sampling and separation

Claes Brage, Qizhuang Yu, Guanxing Chen, Krister Sjöström, "Use of amino phase adsorbent for biomass tar sampling and separation", Fuel Vol.76, No. 2, pp. 137-142, 1997.

Offline methods

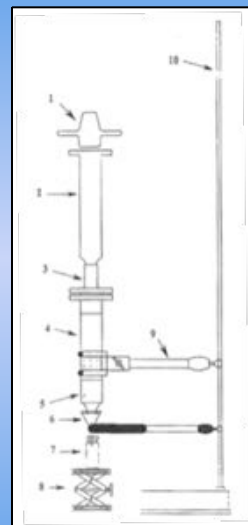
Solid Phase Adsorption (SPA)

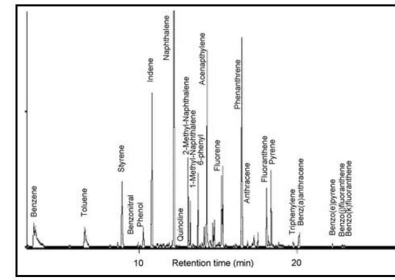


1 = to syringe or electrical pump; 2 = adapter (polypropylene); 3 = sample reservoir; 4 = sorbent tube (PP, 1.3 OD x 7.5 cm); 5 = fritted disc (20 mm polyethylene); 6 = amino-phase sorbent (40 mm, 60 Å); 7 = rubber/silicone septum; 8 = septum retainer (polypropene); 9 = “Tee”-adapter (glass); 10 = syringe needle (stainless steel); 11 = producer gas.

Offline methods

Solid Phase Adsorption (SPA)





Sampling

"T", needle, $SPE\text{-}NH_2$ tube and 100 ml syringe.

Custom made reversible SPE tube.

Sampling of 100 ml in 1 min.

Sample storage

The SPE tube is capped in both ends after sampling.

Samples stored in a fridge/freezer

Sample preparation

Elution for aromatic and phenolic compounds

Chemical analysis

GC-FID - Gas chromatograph with flame ionisation detection

Results

Detection limit: 2.5 mg/Nm^3 (for detectable tars)

Offline methods

Challenges of SPA Method

- Inleakage of air, especially for sub-atmospheric pressure systems
- Using temperature high enough to avoid tar condensation yet low enough not to melt septum
- Plugging of needle by septum material
- Condensation of tars in needle of syringe
- Undesirable heating of SPE column during sampling due to temperature, steam condensation

- **Breakthrough of light tars (BTX)**
- **Desorption of light components from SPE cartridge during storage**
- Efficient elution of aromatic and phenolic compounds
- **Inability to measure heaviest tars**
- **Consistency of procedures for sampling and analysis**

Offline methods

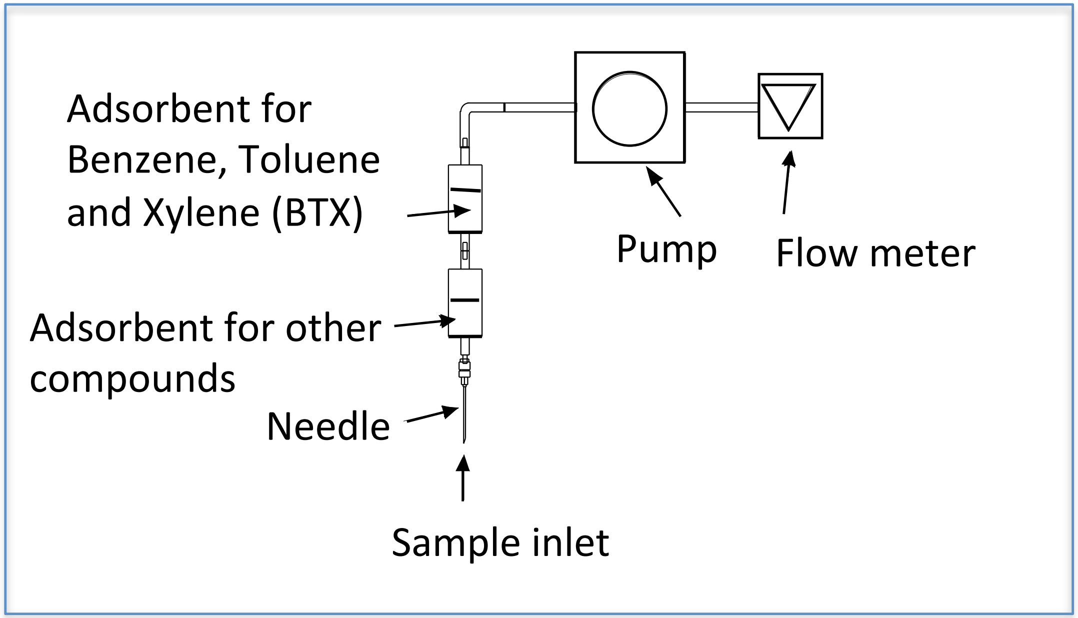
A (biased?) comparison between SPA and “Tar guideline”

Cold solvent trapping (CST) (”*Tar guideline*”)	Traditional SPA (“KTH”)
Advantages: - Gives total tar, heavy and light tar **Drawbacks:** - Time consuming, sampling as well as analysis - Large solvent volumes - Not suitable for (very) low tar concentrations - Low precision	**Advantages:** - Uncomplicated and fast sampling - Low cost - High accuracy and reproducibility - Sampling and analysis can be done separately **Drawbacks:** - Not suitable for heavy tars - B(TX) must be analysed within a few hours

Offline methods

SPA analysis at low tar concentrations and separate BTX analysis (KTH)

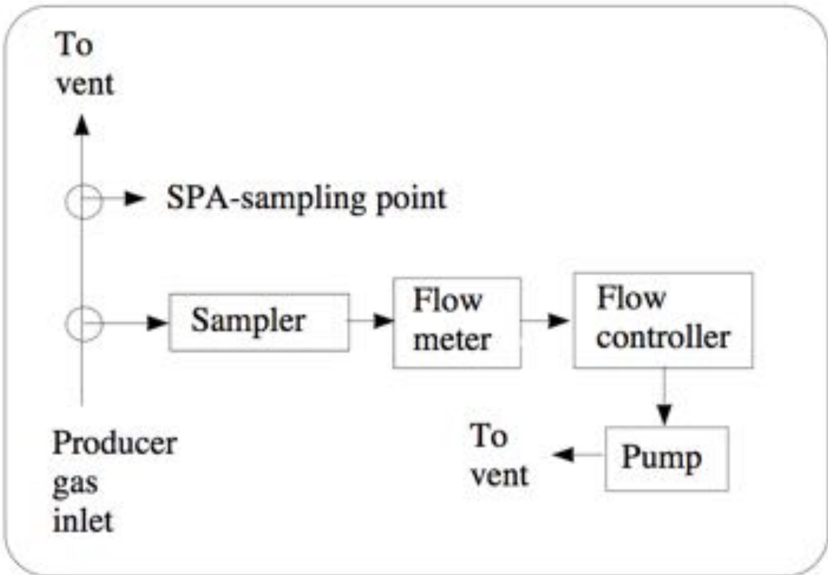
Determination of light tar in low concentrations



"A few other variants exists, e.g. Chalmers and ECN"

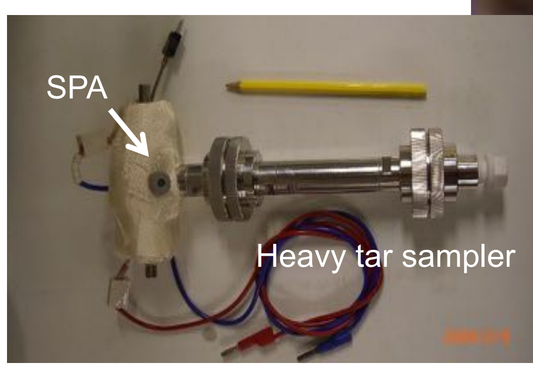
Offline methods

SPA analysis combined with gravimetric tar (KTH)



Sampler mounted on atmospheric fluidised bed gasifier

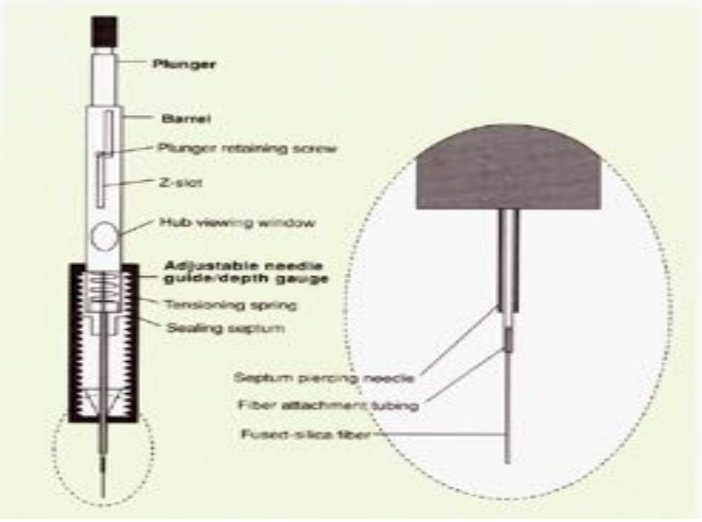
Heated and isolated “T”-connection with SPA-septa (left) and heavy tar sampler (right)



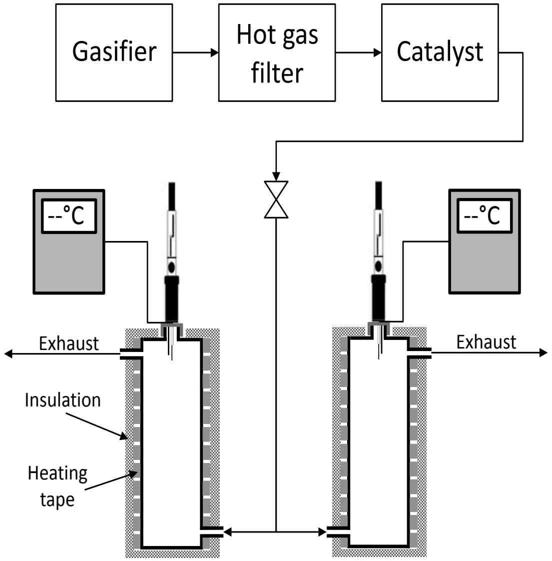
Offline methods

Solid Phase Micro Extraction (SPME)

SPME device



Experimental set-up KTH

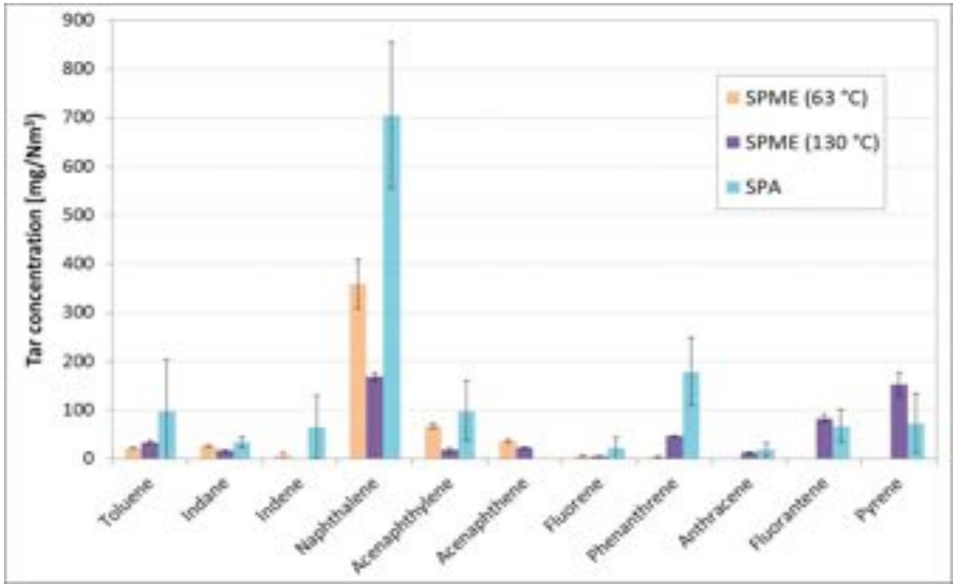


- Method under development
- Extraction of analytes from a sample matrix onto a stationary phase (non polar) - silica fibre with 50 µm polydimethylsiloxane (PDMS)
- Desorption of the analytes in an analytical instrument (GC).
- Developed for low tar content analysis in e.g. syngas applications

Offline methods

Solid Phase Micro Extraction (SPME)

- Tests on real gas with sampling time 10 min.
- The results showed that SPME method is a fast and accurate for low tar concentrations
- Analysis at trace levels below 0.1 mg/Nm^3 (e.g., syngas production) will be possible at 60 °C for all compounds heavier than naphthalene



Brisk report, Advanced measurement methods and operational procedures in thermochemical biomass conversion, D 7.6 Protocols/standards for tar measurement.

Online methods

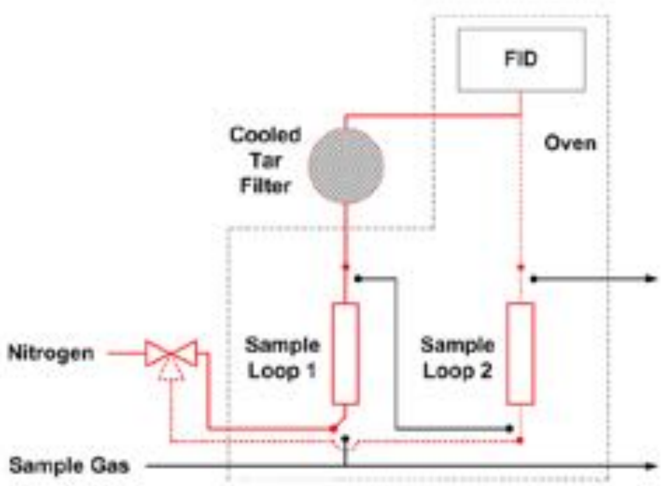
Flame Ionization Detector (FID)

- Prototype developed by researcher at University of Stuttgart.
- The instrument is using FID as a the detector principle.
- The instrument can determine:
  - Total hydrocarbon concentration
  - The non-condensable hydrocarbon concentration
  - The tar concentration

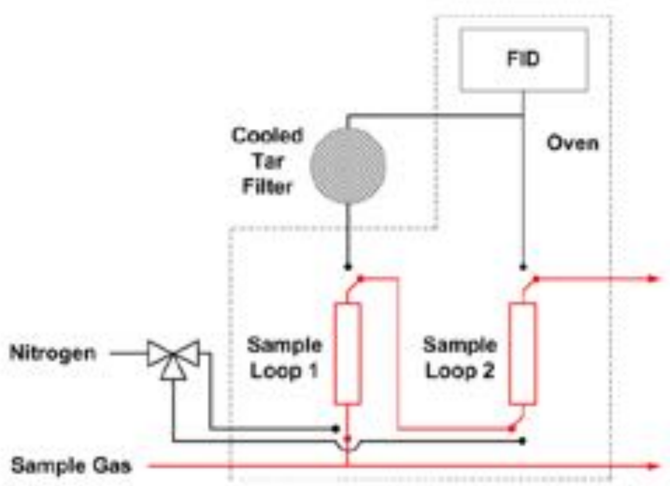
A. Gredinger, D. Schweitzer, H. Dieter and G. Scheffknecht, A Measurement Device for Online Monitoring of Total Tar in Gasification Systems, *J. Energy Resour. Technol* 138(4), 042205

Online methods

Flame Ionization Detector (FID)



Analyzing phase



Sampling phase

Measurement principle:

Difference measurement of the organically bound carbon in the sample gas of two sample loops with equal volume.

Online methods

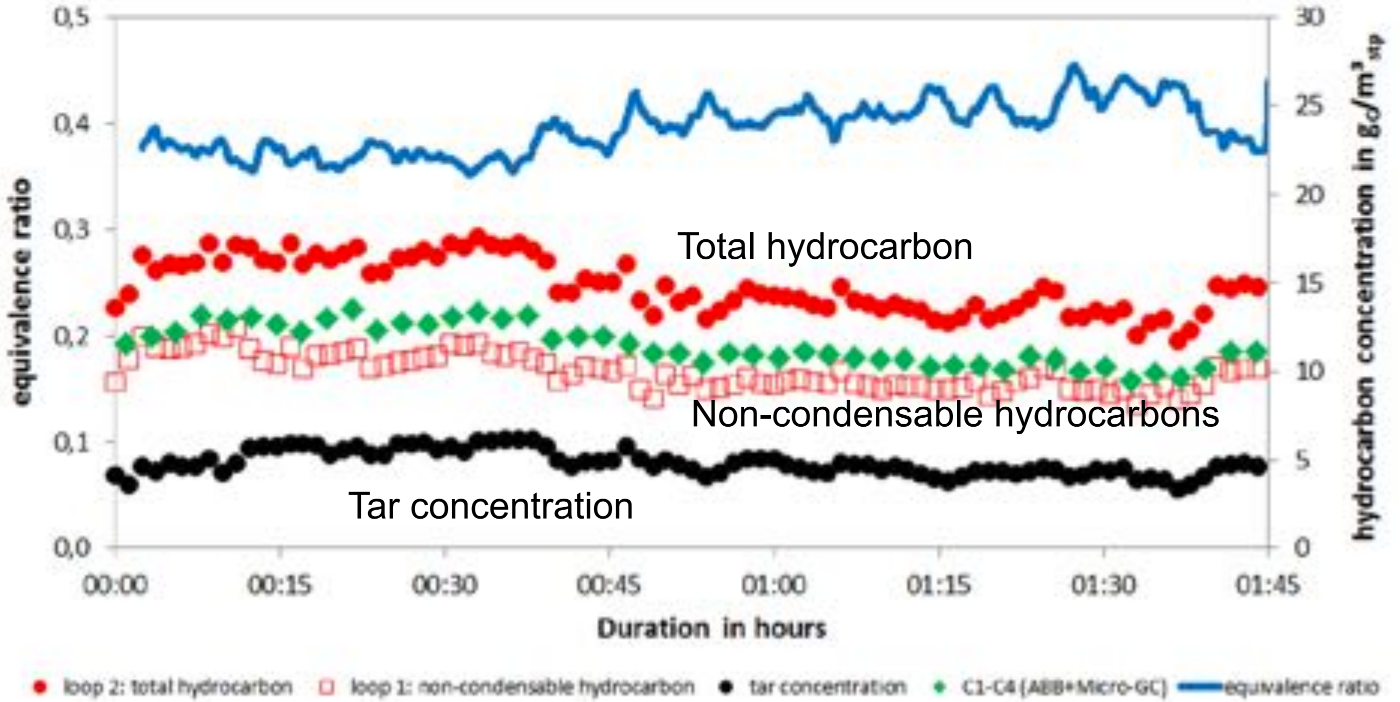


Fig. 9 Results of first field test with real producer gas from gasification

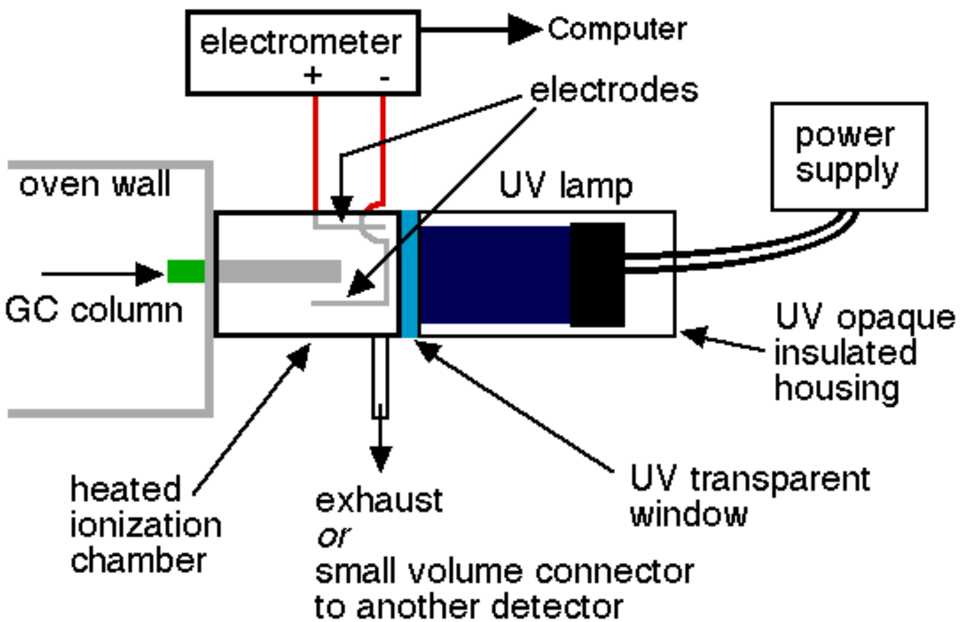
General impression:

- Easy to use
- Provide accurate results in comparison with ”Tar protocol”
- The choice of a suitable tar filter material for the difference measurement was identified as one of the major challenges to gain realistic results.

Online methods

Photo Ionization Detector (PID)

”Method under development at KTH”



A molecule with an ionization potential (IP) lower than the actual energy ($E = hv$) of a photon is ionized.

$$R + h\nu \longrightarrow R^{+} + e^{-}$$

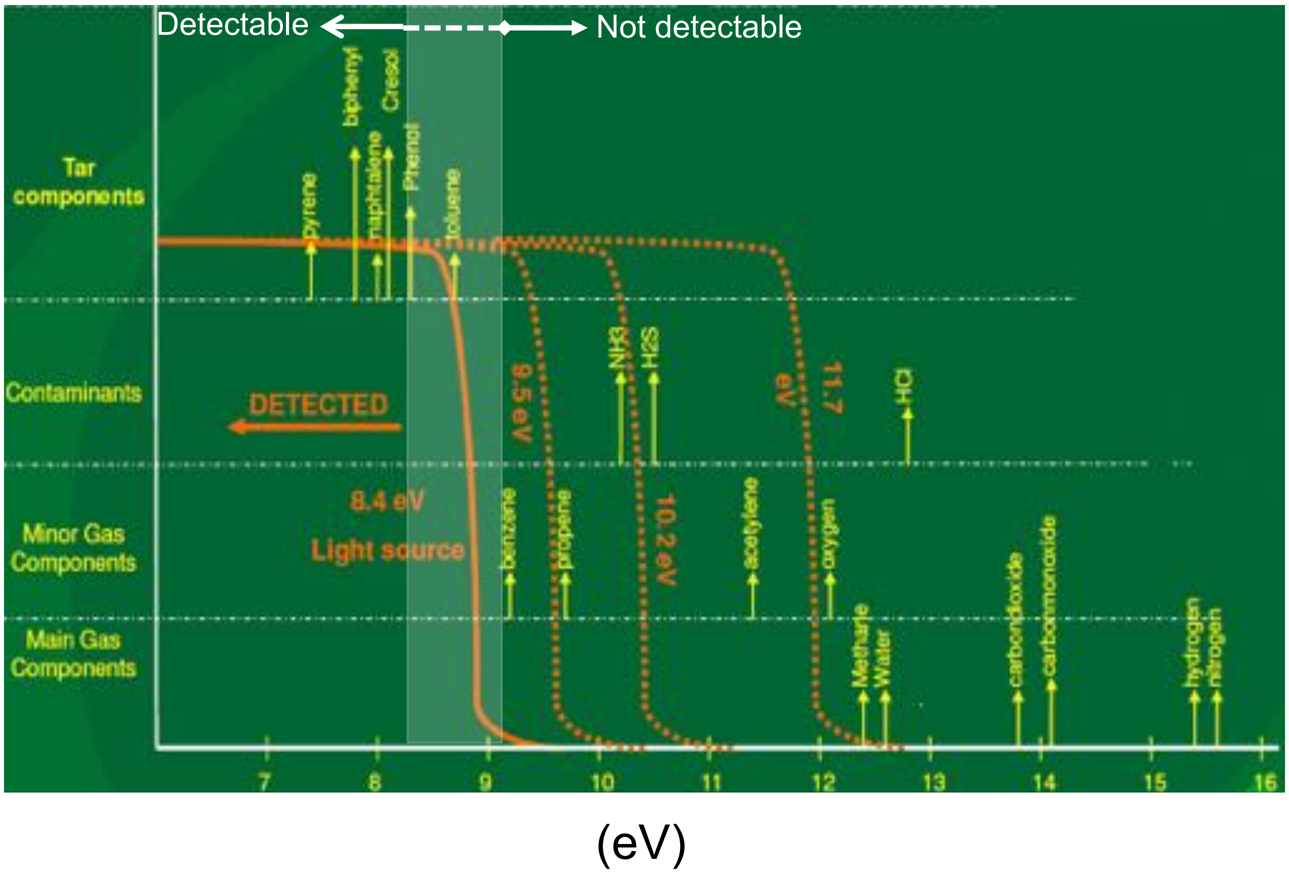
Energy required to remove an electron is different for each compound.

Typical tar compounds require relatively little energy

Possibly a selectivity can be achieved.

Online methods

Photo Ionization Detector (PID)



Energy of the light depends on the gas inside the lamp

Xenon = 8.4 eV

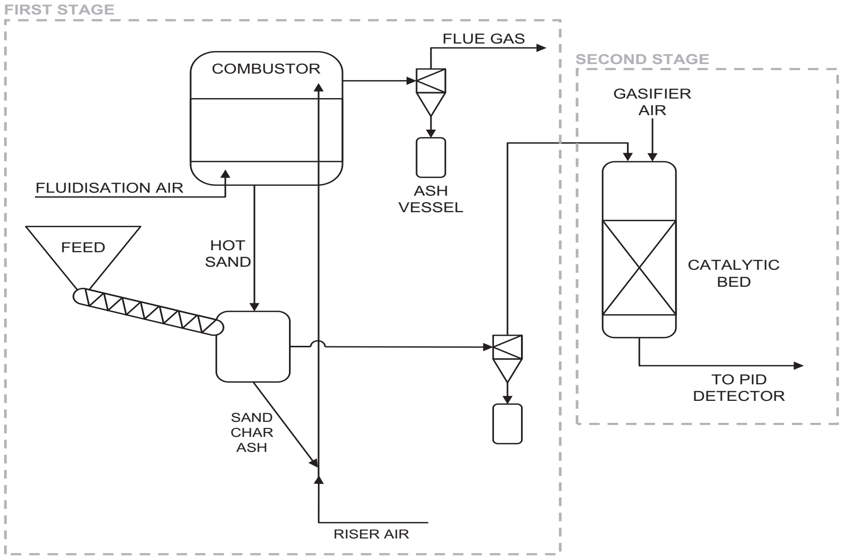
Aromatic compounds with IP < 8.4 eV can be detected, e.g.:

- Naphthalene
- Acenaphthene
- Flourene
- Anthracene
- Pyrene

Online methods

Photo Ionization Detector (PID)

PID in a real gas stream



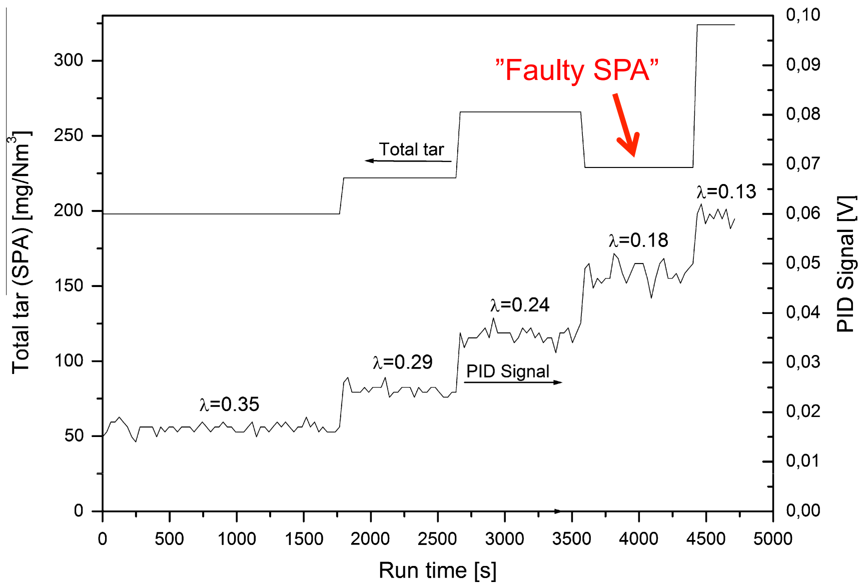
Schematics of the tar measurement system for real gas tests at BTG

Ahmadi M, Knoef H, Van de Beld B, Liliedahl T, Engvall K (2013) Development of a PID based on-line tar measurement method - Proof of Concept. Fuel 113: 113-121.

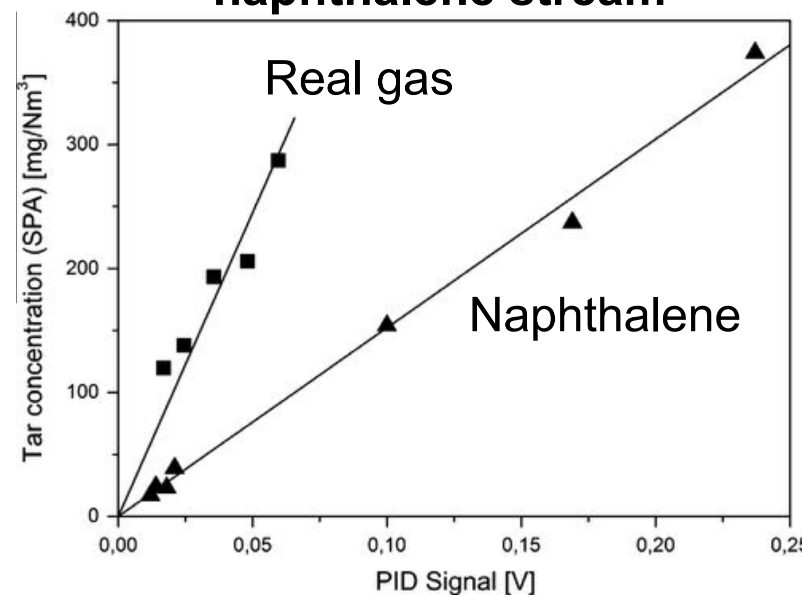
Online methods

Photo Ionization Detector (PID)

PID in a real gas stream



Real gas stream vs pure naphthalene stream



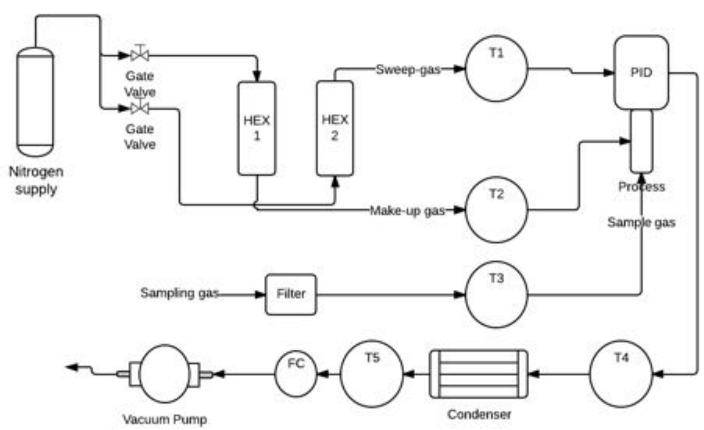
- The PID signal follows the SPA signal at almost all different tar levels
- Both real gas and naphthalene PID signal shows a linear correlation comparing with SPA tar content

Online methods

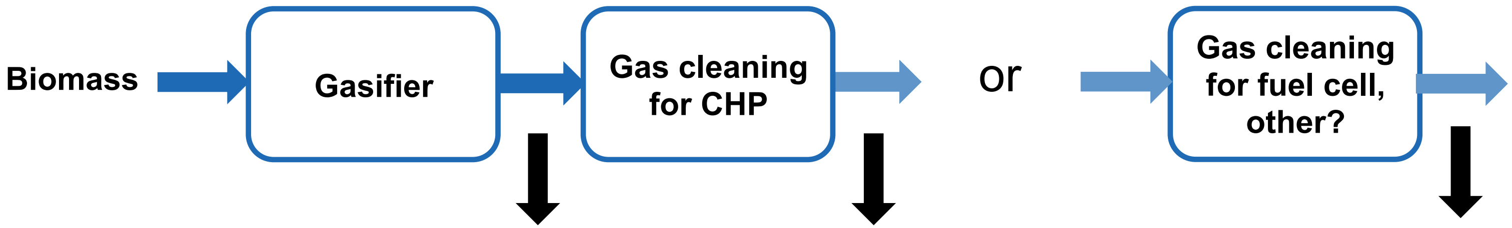
Photo Ionization Detector (PID)

Some observations:

- Different response curves of the compounds will make quantification less accurate during analysis of real producer gas
- Fouling of UV lamp window with time is an issue.
- PID prototype test system developed to address the window fouling problem
- Prototype tests in progress



What is the conclusion?



	High tar (10-50 g/Nm^3)	Medium tar level (5-50 mg/Nm^3)	Low tar Below dew point: 0.1 mg/Nm^3 at 100 °C
Offline	• SPA • Tar protocol	• SPA • Tar protocol	• SPME
Online	• PID • FID	• PID • FID	No viable technique

Summary

Summary

- Simple, low-cost, yet robust means of measuring and characterizing tars is desirable, especially for small scale systems
- Impinger-based method of standard tar protocol is relatively robust but time consuming and laborious
- SPA method much simpler and equally as good for many situations, but does have drawbacks
- Continued development of SPA procedure will improve robustness and utility of the method
- Developed FID and PID under development are both promising candidates for future industrial online tar monitoring

Thank you!

E-mail: kengvall@kth.se