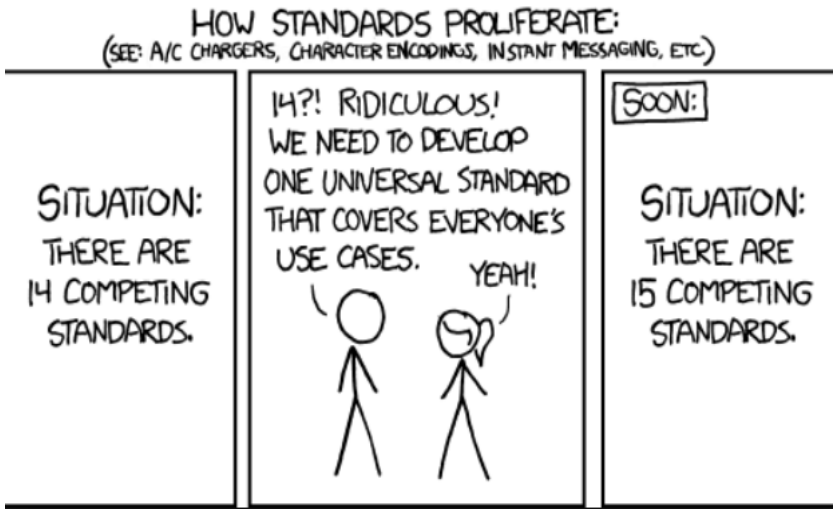
Tar measurements

–

developments towards further standardization



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Wiebren de Jong
TU Delft (NL)

Biofuels Research Infrastructure for Sharing Knowledge

www.briskeu.com

WP 7 *Advanced measurement methods & operational procedures in thermo-chemical biomass conversion*

Task 7.2 Tar sampling & analysis (KTH,ECN,JRC-IE,TUD)

Towards standardized analysis technique(s):

optimal sampling conditions for particle removal, flow, temperature under challenging biomass gasification conditions, moreover analysis

- KTH: on-line PID, heavy tar sampling & analysis, comparison with SPA sampling & GC analysis
- ECN: tar standard & SPA adaptations, (on-line dew point analyser)
- JRC-IE, GC-size exclusion, UV Fluorescence (heavy tar)
- TUD: online GC-FID/FID, BTX optimized SPA

➡ pave the way for development of less elaborate, on-line?? practices via new protocols and following benchmarking! WP5 Protocols, Databases and Benchmarking

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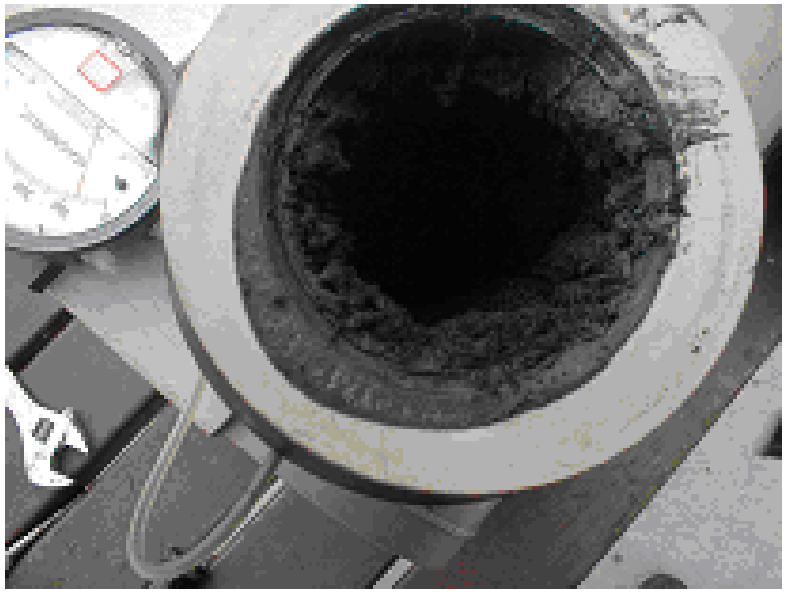
Tar, what is it?

- **In the end of the nineties (last century) long discussions in scientific community (a.o. IEA, EU-FP5) 'ending' in:**

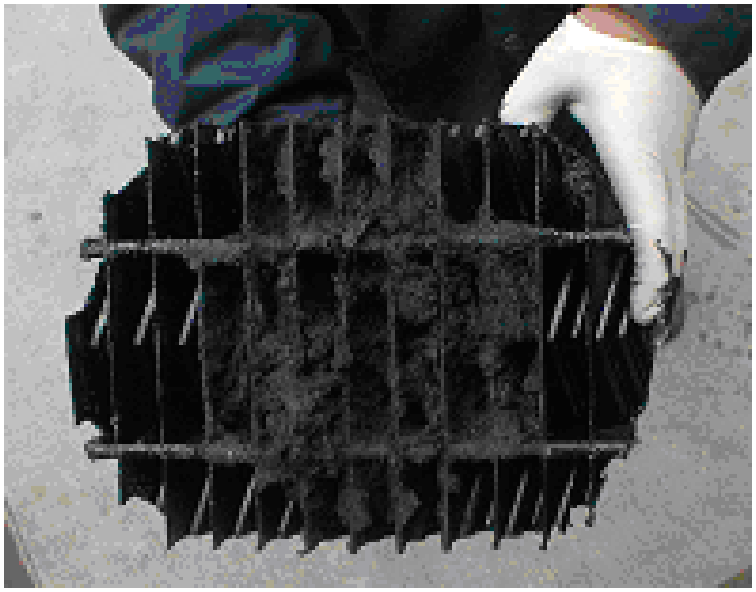
Generic (unspecific) term for entity of all organic compounds present in the gasification product gas excluding gaseous hydrocarbons (C1 through C6)

What are the issues with tars?

Relatively low temperature gasifiers (FixB, [C]FB) cause tar issues (next to gasification product gas losses):



Pipe blocking



Process Equipment Fouling

→ Need to measure tars

HOW??

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Courtesy: www.thersites.nl (ECN)

Tars classification

Most relevant in dew point

Most relevant in water pollution

Class	Type	Examples
1	GC undetectable tars.	Biomass fragments, heaviest tars (pitch).
2	Heterocyclic compounds. These are components that exhibit high water solubility	Phenol, cresol, quinoline, pyridine.
3	Aromatic components. Light hydrocarbons, which are important from the point view of tar reaction pathways, but not in particular towards condensation and solubility.	Toluene, xylems, ethyl benzene (excluding benzene.)
4	Light poly-aromatic hydrocarbons (2-3) rings PAHs). These components condense at relatively high concentrations and intermediate temperatures.	Naphthalene, indene, biphenyl, antracene.
5	Heavy poly-aromatic hydrocarbons (>4-rings PAHs). These components condense at relatively high temperature at low concentrations.	Fluoranthene, pyrene, crysene.
6	GC detectable, not identified compounds.	Unknown

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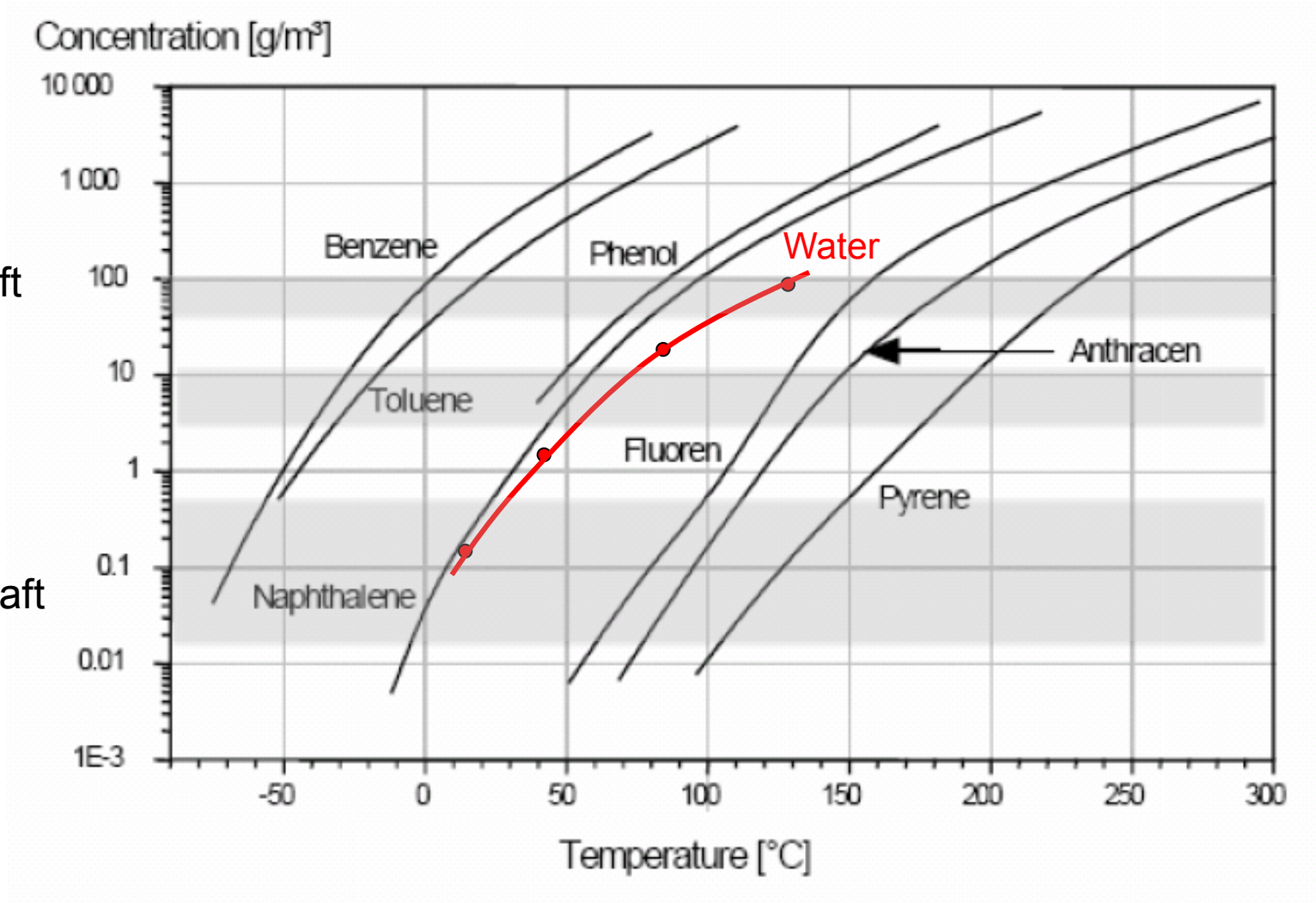
Equilibrium tar concentration vs. dew point

Updraft

FBG

Downdraft



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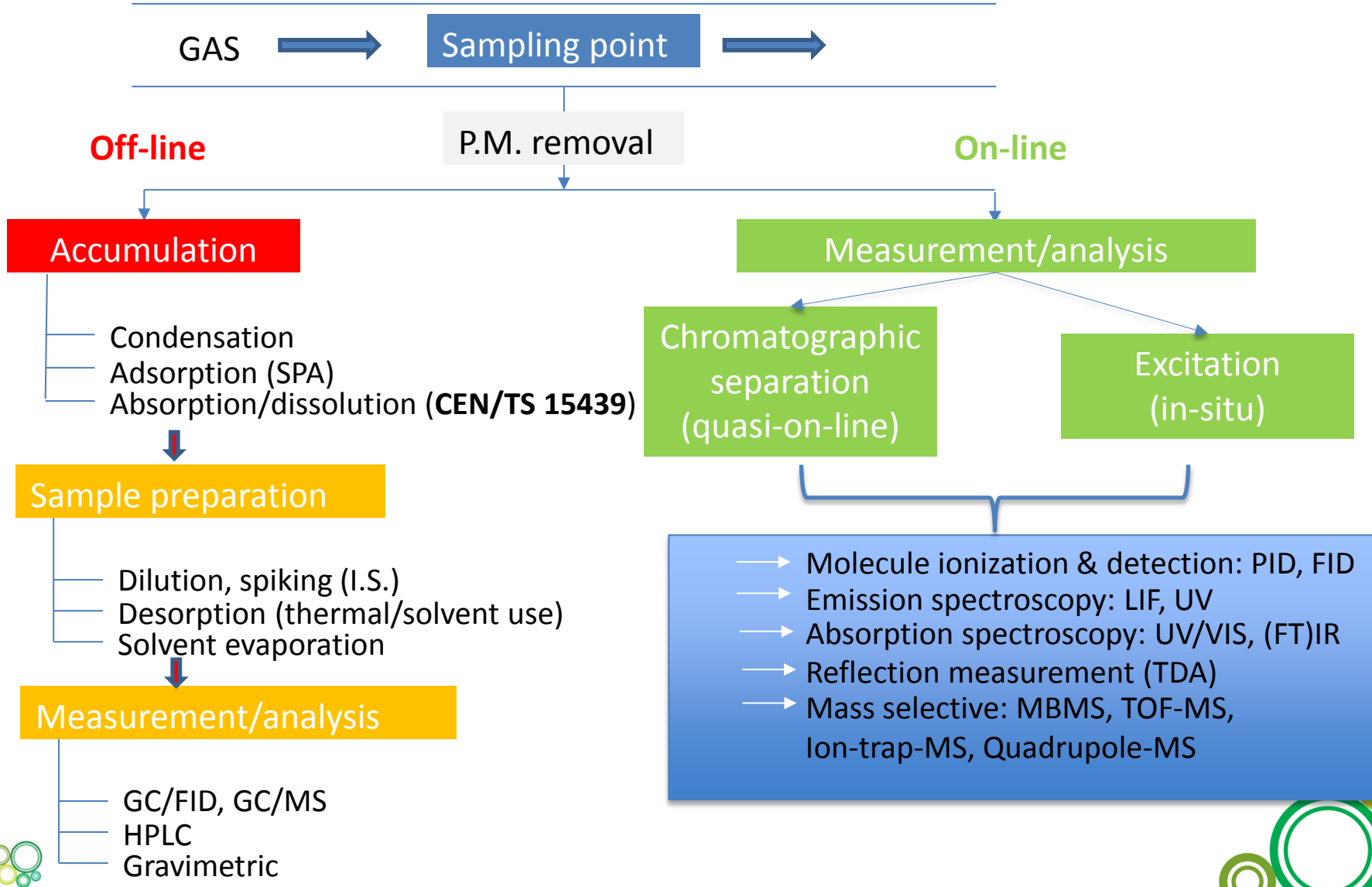
Questions, for a workshop on tar …

- **What do we want to know with respect to tars in the produced gases from biomass gasification?**
  - **Just their condensation behavior (= issue) under certain process conditions (P, T) → dewpoint**
  - **Aromatic organic species distribution? From which threshold value?**
    - **Sampling ex- versus in-situ? frequency? On/off-line?**
    - **Detection frequency? On/off-line?**

- **Boundary conditions of Safety, Costs, Labor intensity …**

"After closer investigation, it's become clear that we need to enter more than one value."

Generic diagram for tar sampling & analysis



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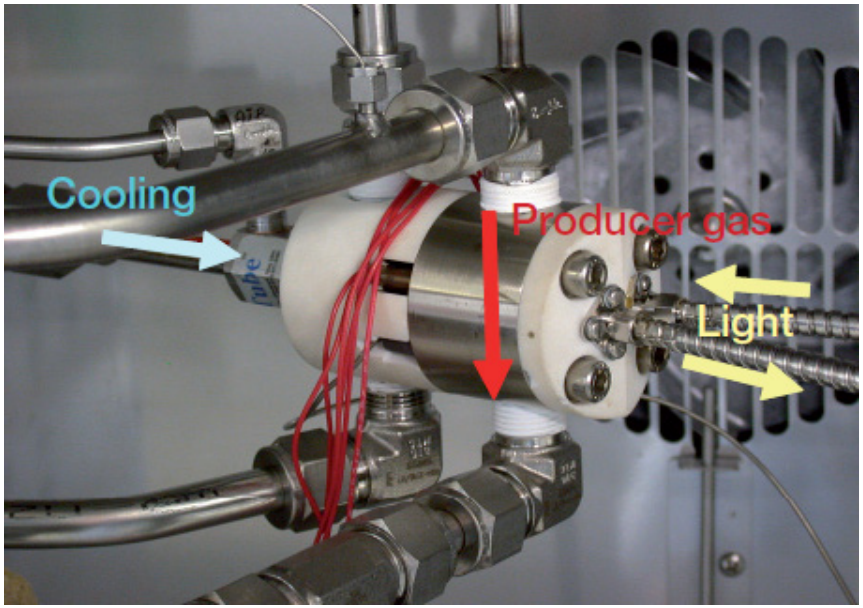
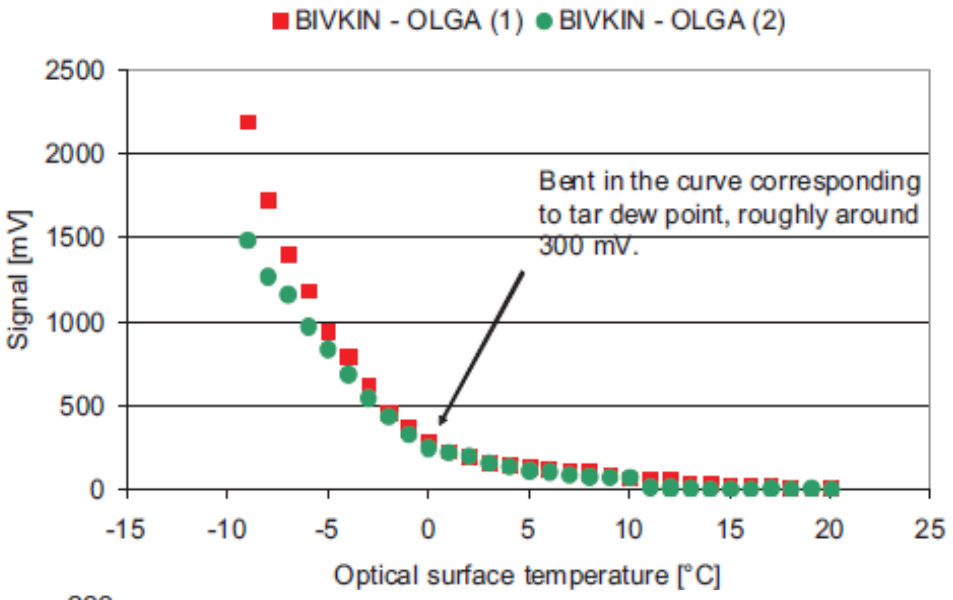
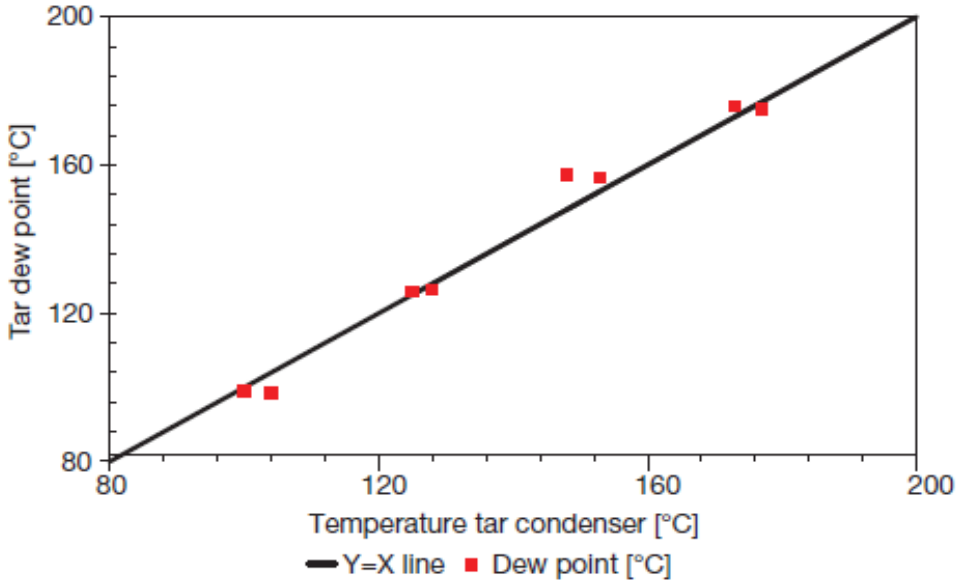
Adapted from Knoef et al., in Handbook Biomass Gasification 2nd edition 2012

When only condensation matters
Tar Dew Point analyzer (ECN) a possible solution







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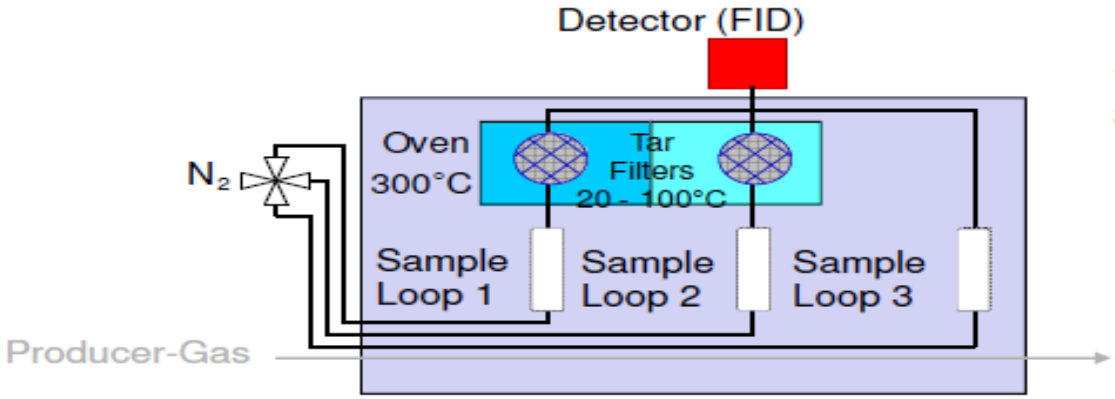
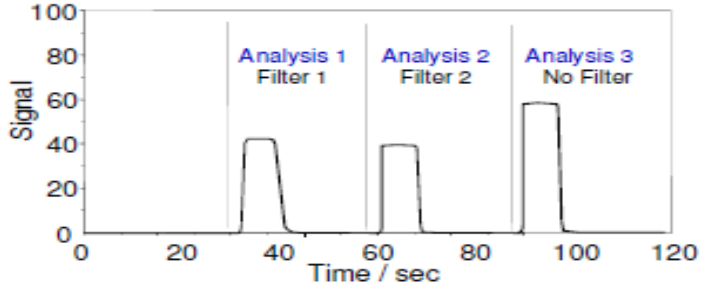
See www.thersites.nl

Another on-line tar analyser, based on tar condensation & FID detection: the OTA (IFK)





Goal: Measure the content of condensables carbon (tars)

$$C_{cond} = Peak_3 \cdot R_3 - Peak_{1/2\ ave} \cdot R_{1/2\ ave}$$

$Peak_{3,1,2}$: FID Signal
$R_{3,1,2}$: Response factor

Calculate the response factor => calibration with Methane (5 Vol-%)

$$R^* = \text{C-concentration of the calibration gas [mg/Nm}^3\text{] / Peak}$$

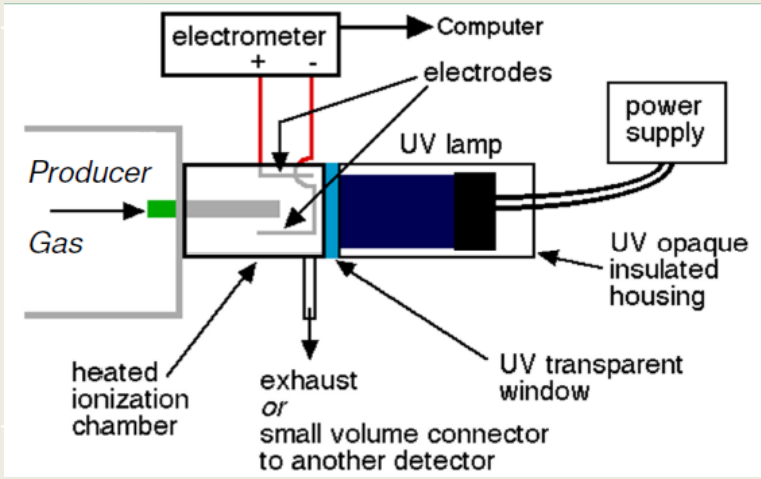
C-concentration of the calibration gas [mg/Nm³]:
5 Vol-% · density [kg/m³] · C-content [kg C/kg] · 10^6 [mg/kg]

C-concentration of the calibration gas = 26925 [mg/Nm³]

Different filter types and temperatures give global, <u>total condensables</u> indication relatively fast response time -> 'dynamic' measurements!

Source: http://www.evur.tu-berlin.de/menue/forschung/veranstaltungen/tar_workshop/
Presentation by Poboss (IFK, Stuttgart), European Biomass Conference 2011, Berlin

KTH – Novel tar analysis method based on on-line photo ionisation detection (PID)



DETECTABLE

Most likely detectable

NOT DETECTABLE

Tar components

Pyrene

Biphenyl

Naphtalene

Cresol

Phenol

toluene

Contaminants

9.5 eV

NH_3

H_2S

11.7 eV

HCl

Minor Gas Components

8.4 eV

Light source

benzene

propene

10.2 eV

acetylene

oxygen

Main Gas Components

Methane

Water

carbondioxide

carbonmonoxide

hydrogen

nitrogen

7 8 9 10 11 12 13 14 15 16

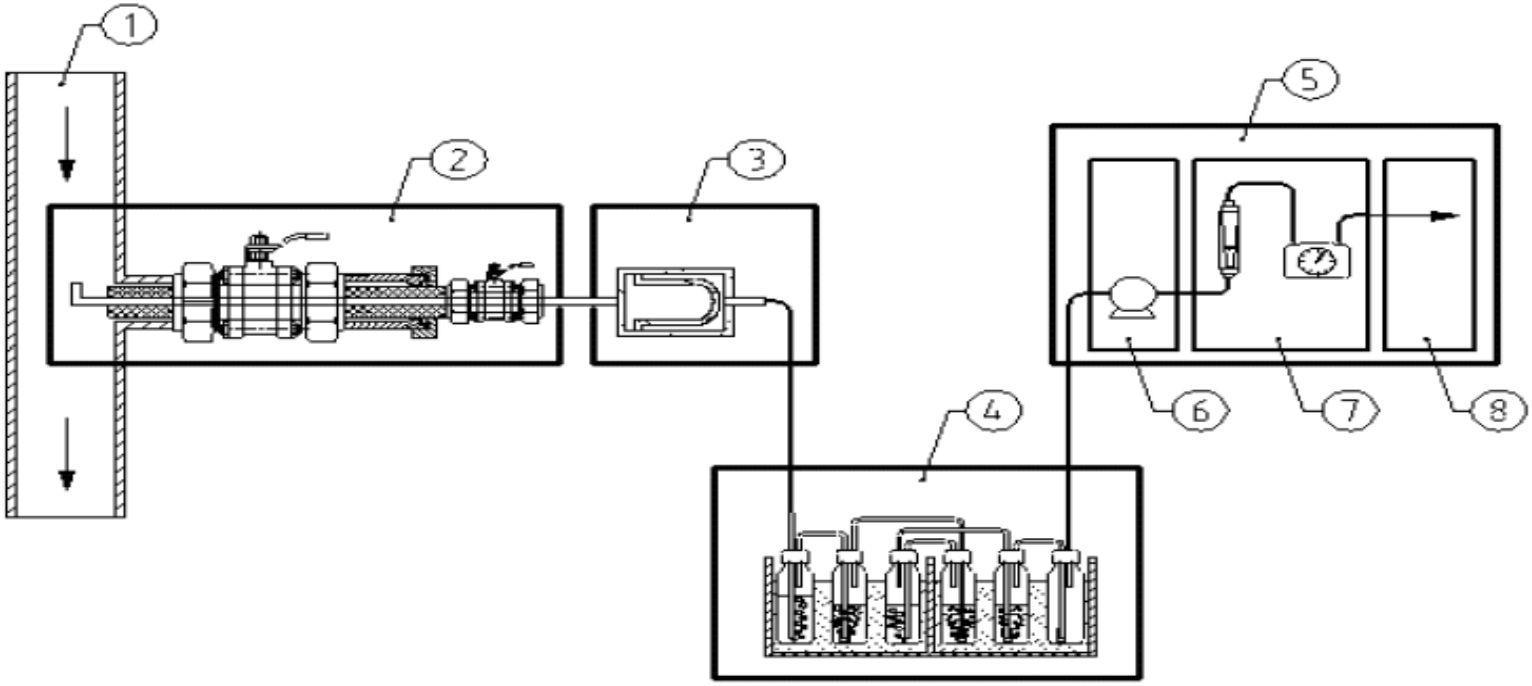
Ionization potential (eV)

Source: http://www.evur.tu-berlin.de/menue/forschung/veranstaltungen/tar_workshop/

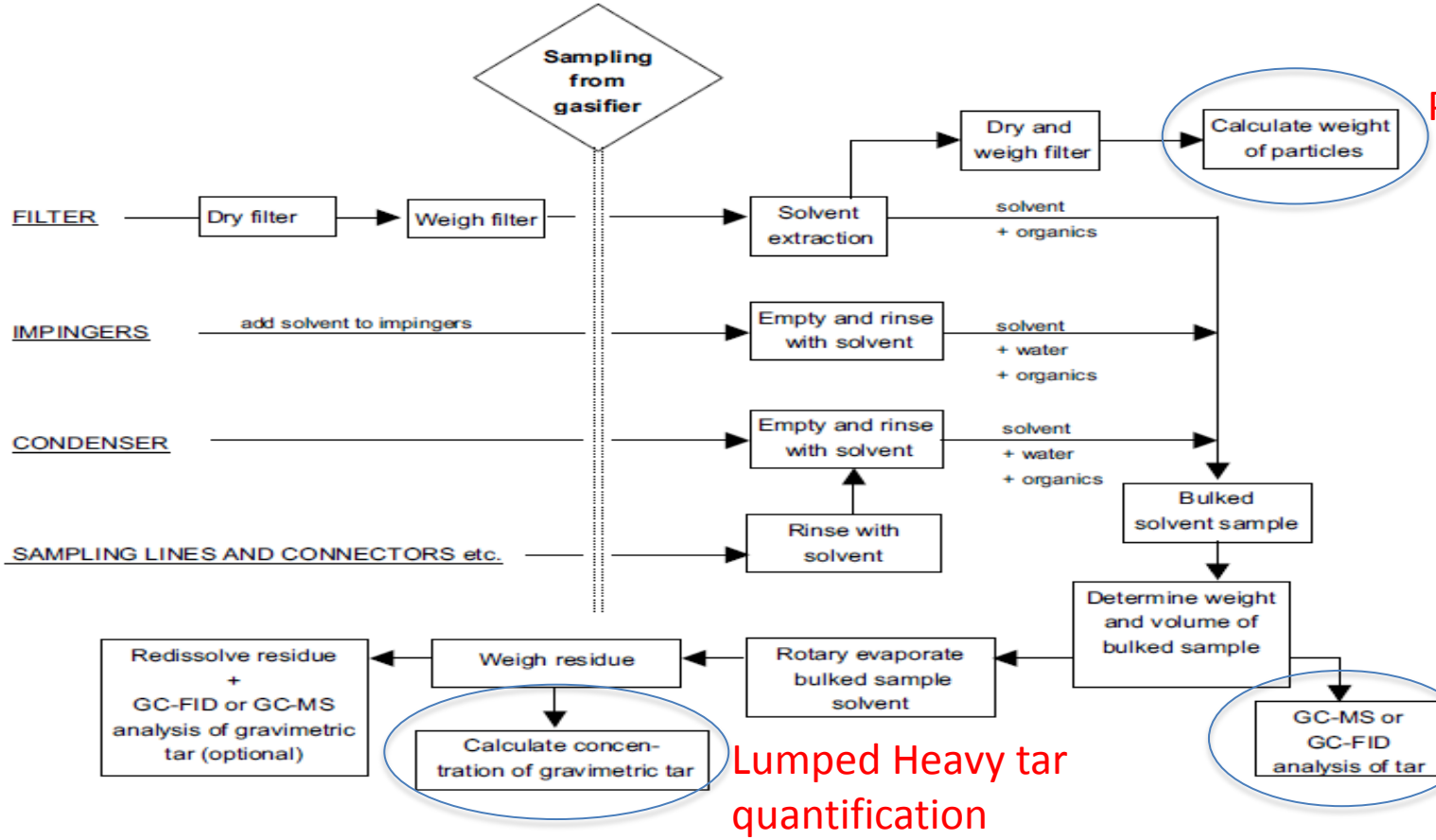
Presentation by Knoeff (BTG, Enschede) in cooperation with KTH, European Biomass Conference 2011, Berlin

Off-line techniques, existing

- **Our benchmark so far: CEN/TS 15439**
  - + Current standard in Europe, thus well-defined, described, tested
  - + Provides quality and quantity of heavy and light tars up to species level
  - - Labor intensive -> costs
  - - Slow regarding sampling AND analysis



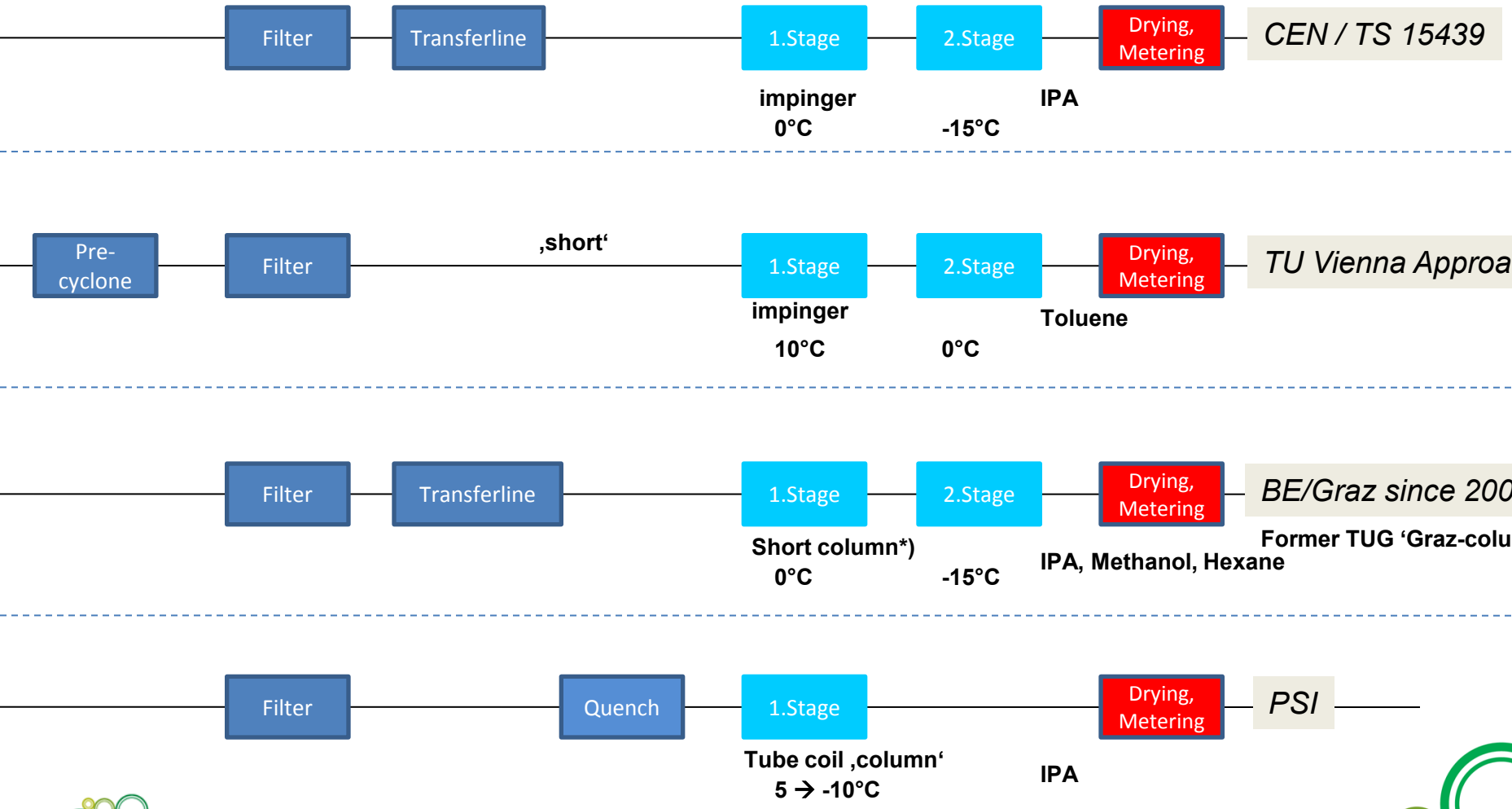
Picture from CEN/TS 15439



Post-treatments

Picture adapted from CEN/TS 15439

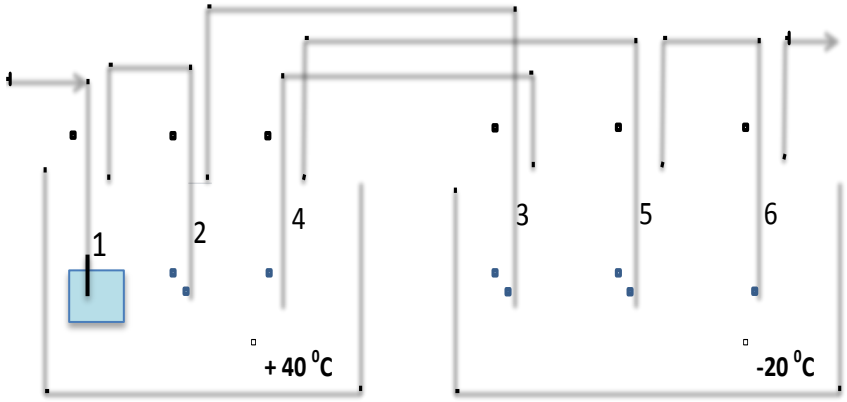
Suitable Concepts - ‘derivatives’ from CEN / TS 15439



Courtesy: Markus Kleinhappl (BE2020+)

ECN setup for product gas sampling

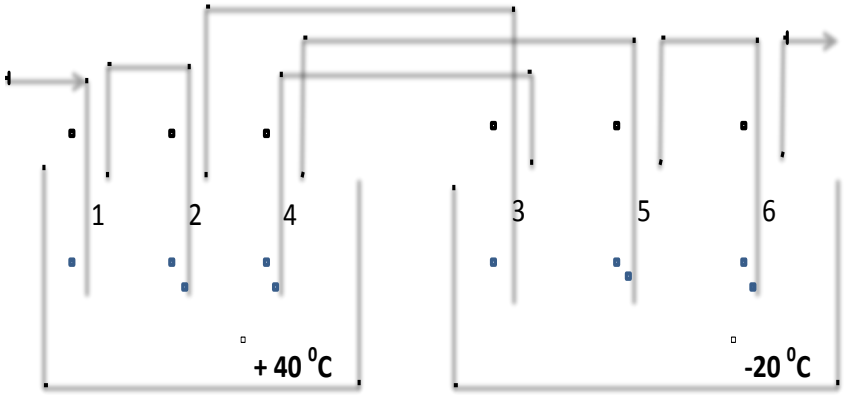
(also suitable for water rich product gas)



CEN/TS: (7.1.2; page 12)

Nr 1: no frit;
nr 2: coarse/fine frit;
nr 3+5+6: medium/fine frit.
Only 1,2,3,4,5 filled with IPA

(Risk of plugging impinger 2 and 3)



ECN setup:
(no problem with high water content of product gas)

Nr 1 **+ 3**: no frit;
nr 2+ 4+ 5: **coarse** frit;
nr 6: fine frit.
All impingers filled with IPA

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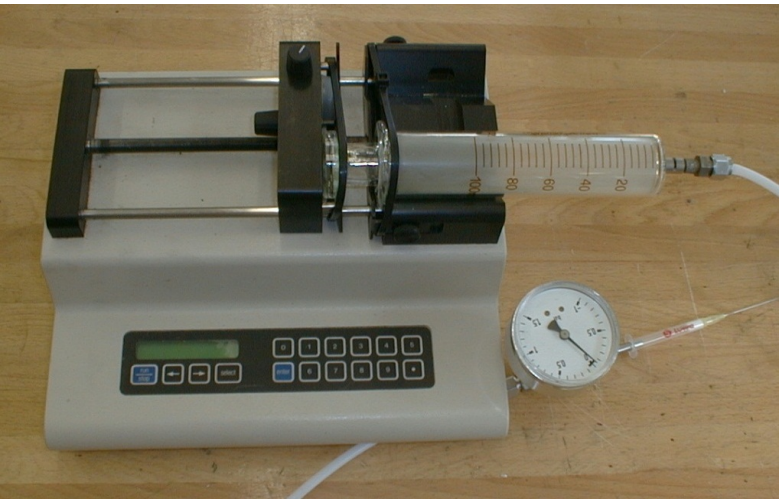
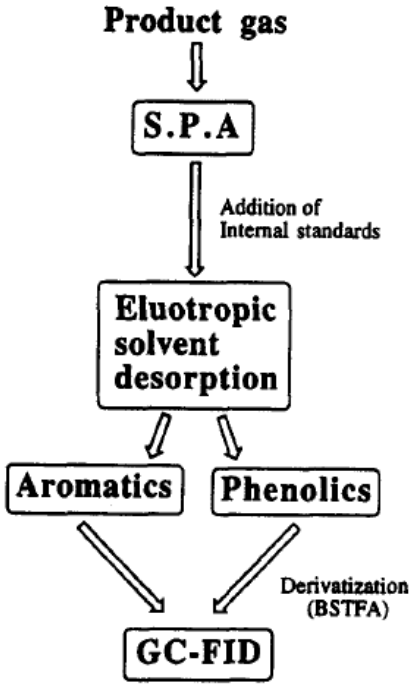
Courtesy: Johan Kuipers (ECN)

Off-line techniques, existing



Solid Phase Adsorption

+ Simple, well-repeatable, fast sampling and elution
+ Samples can be well-preserved for higher, PAH tars
+ Quantification of species
- Slow analysis
- Detection limit might be on the high side



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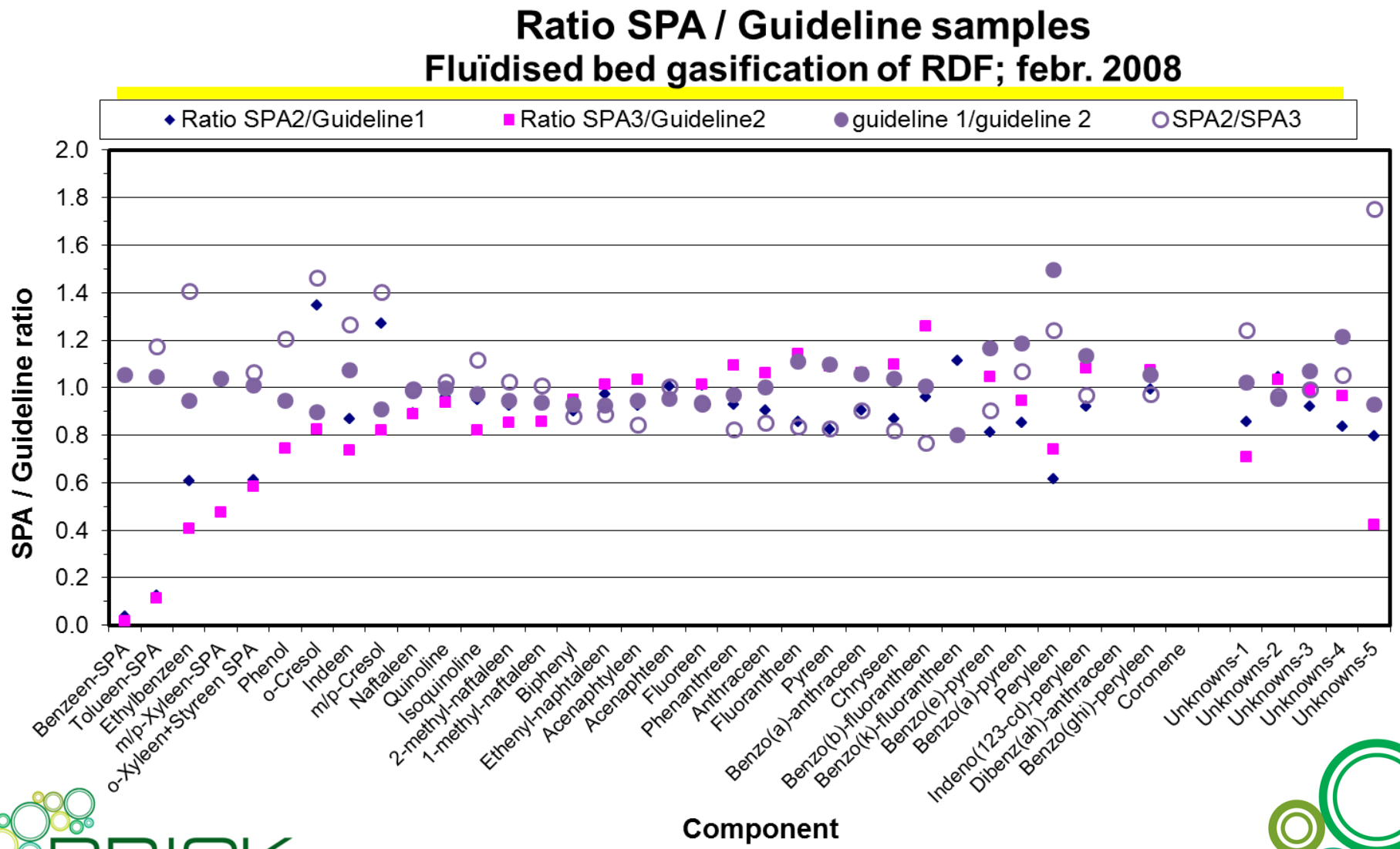
Pictures: courtesy ECN

Schematic from Brage et al. (1997), Fuel, **76** (2), pp.137-142

Comparison of SPA-NH2 with CEN/TS

(SPA samples were not stored in freezer for two days)



Courtesy: Johan Kuipers (ECN)

Intermediate Conclusions

- Using different setup of impingers/frits will help to prevent plugging of frits by fine particles/tar and plugging by ice crystals from condensed water.
- SPA-NH2 and CEN/TS results give comparable results for non-volatile tar components
- SPA-NH2 is not suitable for Benzene/Toluene (volatile); For Benzene/Toluene other SPA phase must be used or use (micro)-GC.

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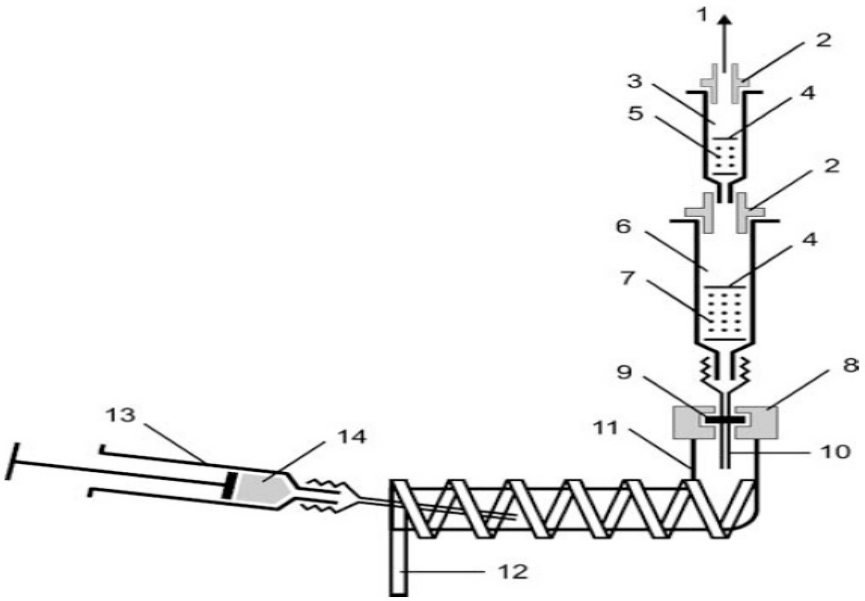
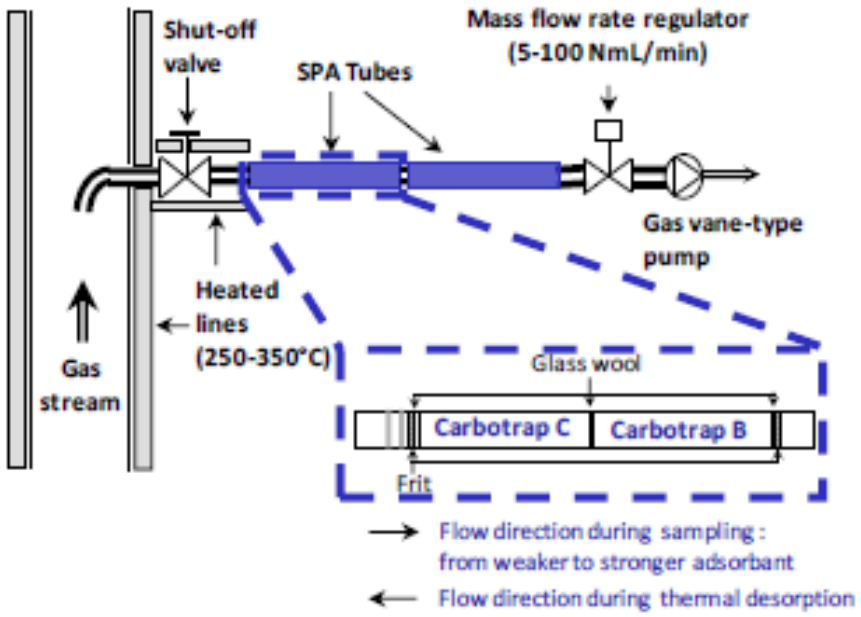
Adaptations to SPA

Series of spa standard tube with charcoal cartridge on top: Enhanced BTX sampling & analysis





Osipovs, S. (2008). "Sampling of benzene in tar matrices from biomass gasification using two different solid-phase sorbents." Analytic and Bioanalytical Chemistry **391**: 1409-1417.

Masson, E., Ravel, S., Thiery, S., Dufour, A. (2011). "Tar analysis by Solid Phase Adsorption (SPA) associated with Thermal Desorption And Gas Chromatography analysis. Pres. at the 19th European Biomass conference, Berlin, 2011.

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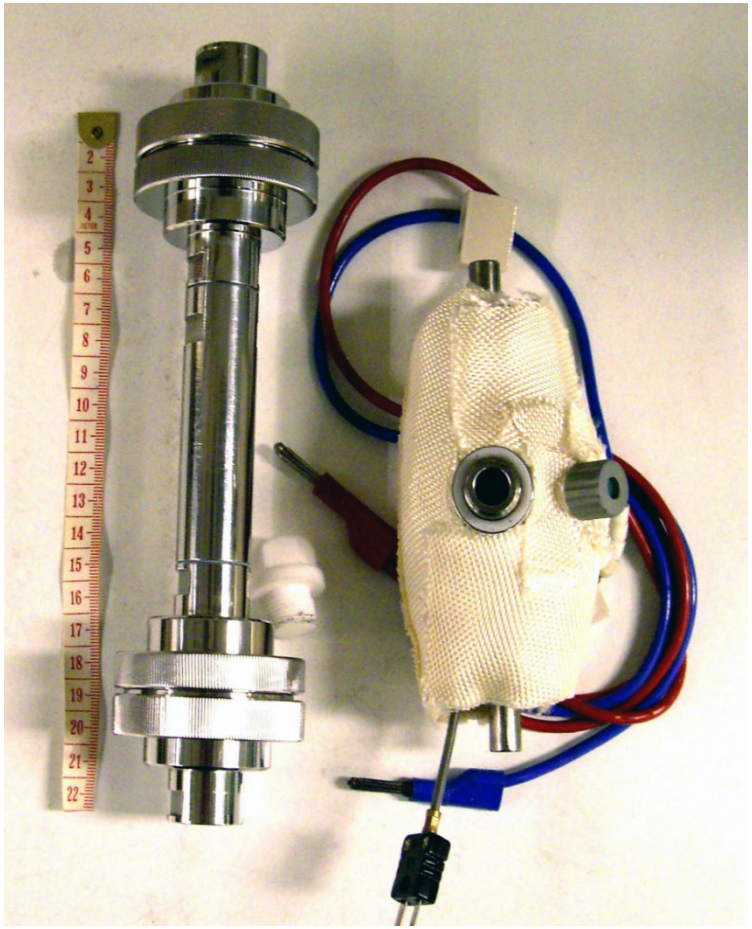
Adaptations related to SPA (KTH)



Heavy tar sampler (left) and heated T-joint (right).

The T-joint allows simultaneous light tar analysis via septum (SPA) and connection to sampler for heavy tar analysis (by weight).

Included also: small gas flow meter and small gas pump.

Heavy tar + light tar = total tar

The method is in principle developed -> to be patented and/or published in near future.

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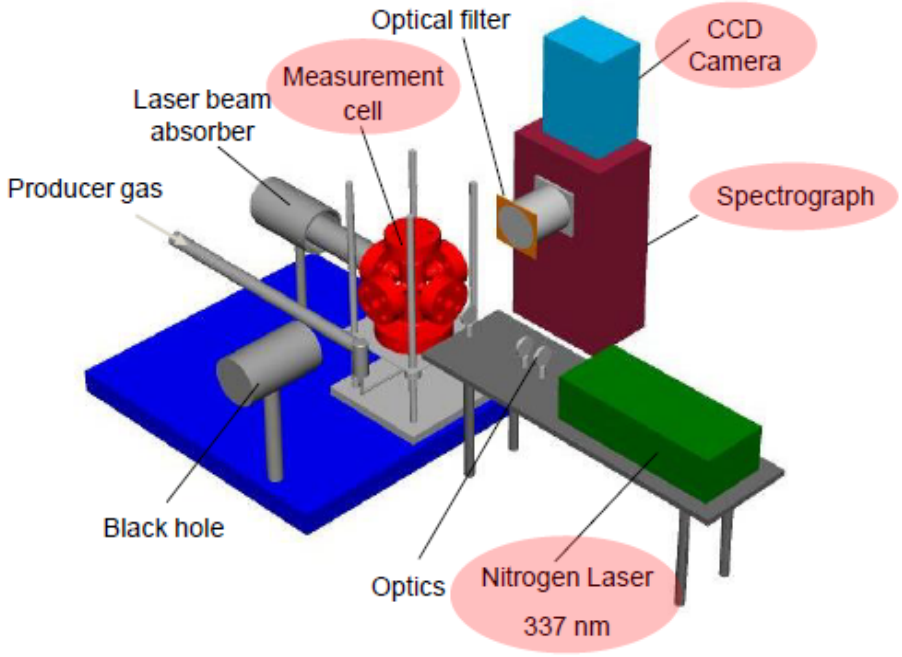
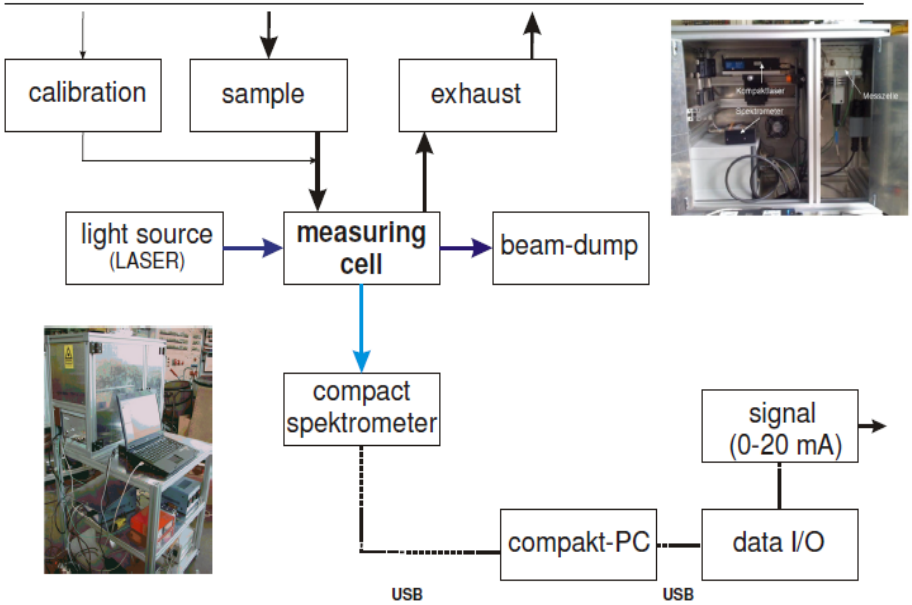
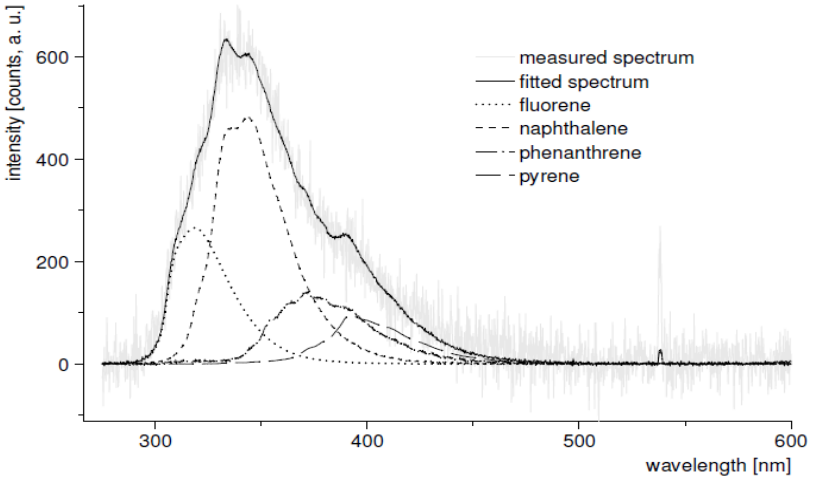
Courtesy: Truls Liliedahl (KTH)

Laser Induced Fluorescence Spectroscopy (TUB/TUM)





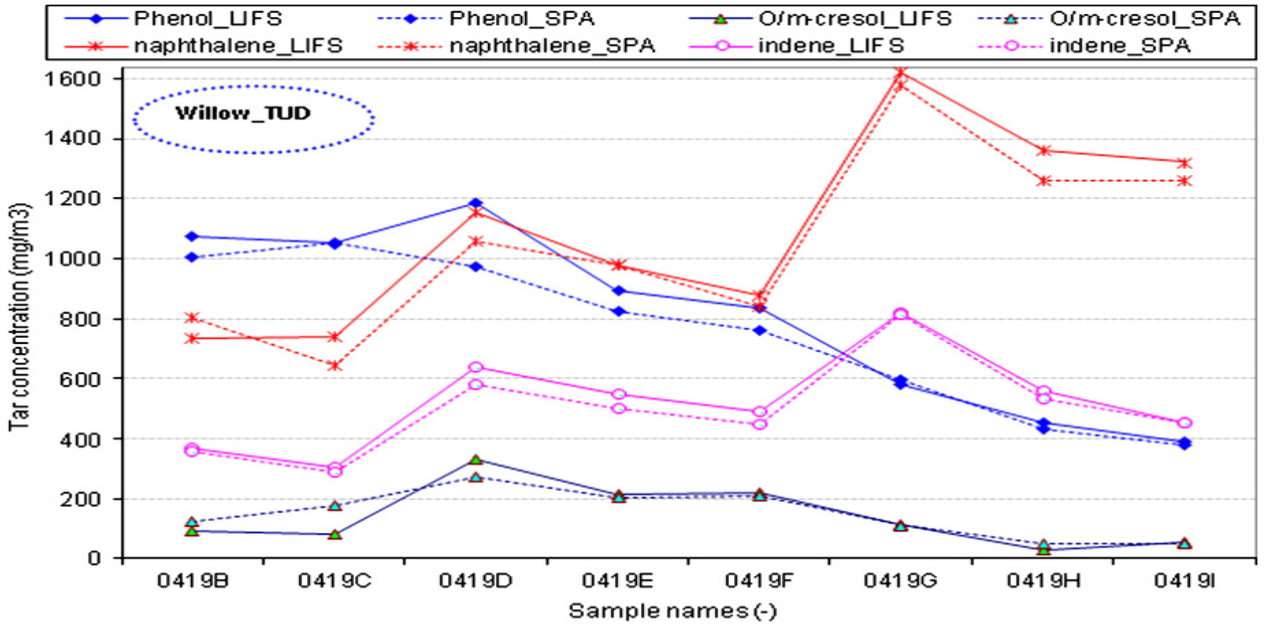
CONTAR – CONtinuos TAR-analyzer

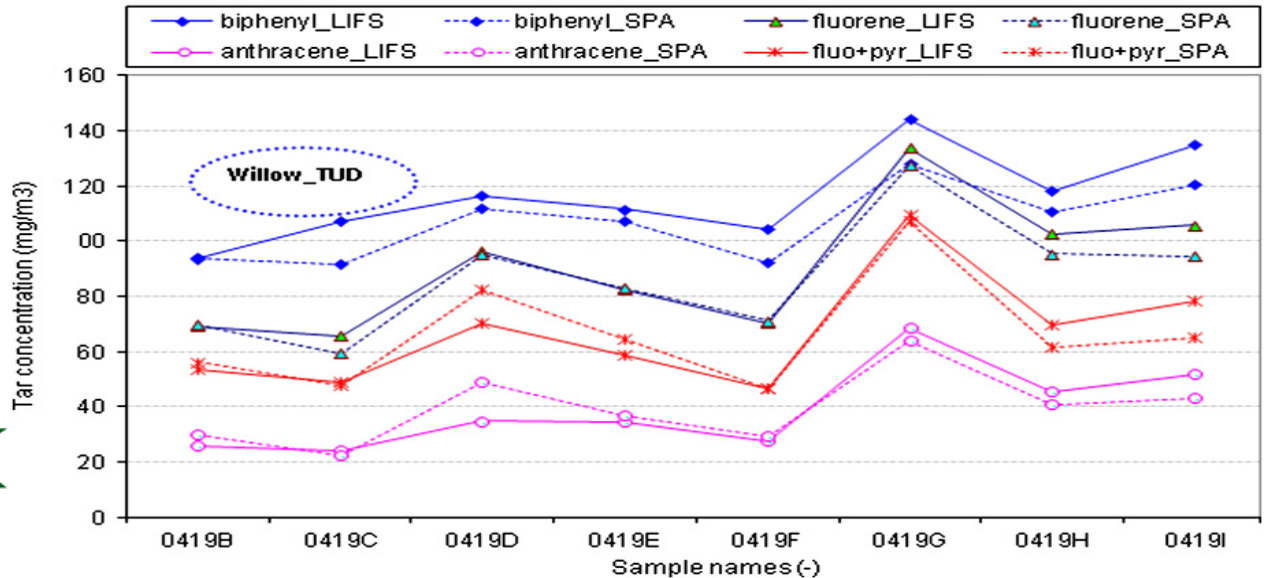


+ In-situ
+ on-line
- Expensive
- Calibration complex, specialist needed

Source: http://www.evur.tu-berlin.de/menue/forschung/veranstaltungen/tar_workshop/
Presentations by TUM (Mayerhofer) and TUB (Zobel), European Biomass Conference 2011, Berlin

Comparison SPA with LIFS – TUD CFB steam – oxygen blown gasifier





Source:
Meng et al. (2012)
Fuel Processing Technology
100, pp. 16-29

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Which items can be updated to CEN /TS?

Improvement of definitions/declarations

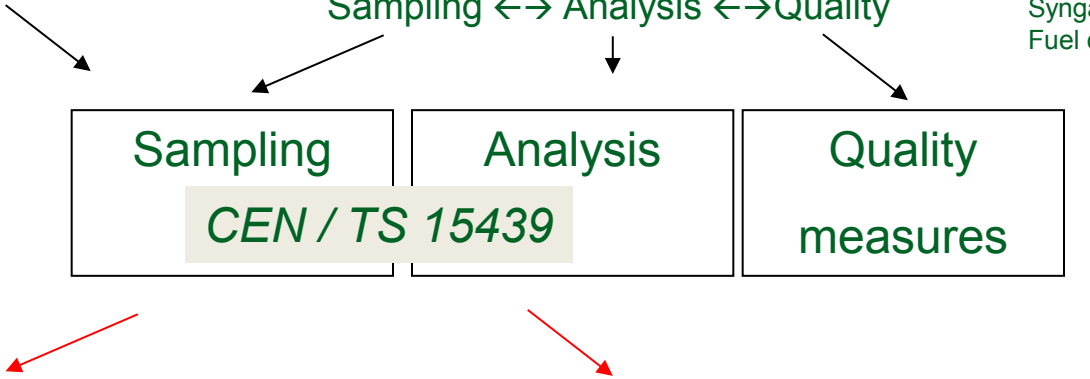
/ Type of Gas
/ Degree of Treatment

Pyrolysis
Types of Gasifiers
Product gas for Engine
Syngas conversion
Fuel cells

/ discrete Components
/ families of compounds (=classes)
/ physically lumped classes
Methodology of
Sampling ←→ Analysis ←→Quality

/ Utilisation target
/ specific recommendations

Burners
Engines
Syngas conversion
Fuel cells



/ Cluster of quality parameters
Particulate/ Aerosol matter
'tar'
'tar-species'
Other
Include/exclude ASH

News:
Filter – elements /cross flow/ dilution methods
Sampling probes (heated)
Particles/aerosols/ classification of solids (T)
Impingers ←→ columns ←→ cont. mass transfer
SOLVENT optimization??
Liquid methods ← → SPE (solid phase)

News:
Off-line / on-line
Detection/Measurement
HPLC/GC-methods
Selective Recovery from SPE
Hyper-systems with toolboxes®
Water detection

Test procedures of capture & analysis
(testgas generators)

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Courtesy: Markus Kleinhappl (BE2020+)