Business from technology

# VTT's observations on tar measurements

Gas Analysis 2013 Workshop

at the 21st European Biomass Conference and Exhibition

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# Validation of the the tar-protocol – reformed ’clean’ gas

- Samples were taken both in isopropanol and dichloromethane.
- The measurements with purified gas (catalytic reforming) gave consistent results with both solvents
  - The measured concentrations were in general well within a 5-% window and there was no systematic difference in the results according to the boiling point or chemical nature of the tar compound.

# Tar-laden ’raw’ gas: IPA and DCM-bottles in series

- Conditions:
  - Filtered “raw” biomass gasification gas (ca. 5 g/$m^3_n$ of tars)
  - Tars were first trapped in isopropanol and the effluent gas was further sampled in dichloromethane
  - Gas flow rate **6 $dm^3_n$/min**
- Observations:
  - Heavier tars did not dissolve completely in isopropanol and in some cases more than 10 w-% of the tars slipped to the dichloromethane phase.

6 $dm^3_n$/min

| Compound | Distribution in solvents, w-% | |
|---|---|---|
| | IPA | DMC |
| Benzene | 100,0 | 0,0 |
| Toluene | 100,0 | 0,0 |
| Styrene | 100,0 | 0,0 |
| Indene | 100,0 | 0,0 |
| Naphthalene | 99,9 | 0,1 |
| 2-Methyl-1-Naphthol | 85,6 | 14,4 |
| Phenanthrene | 90,5 | 9,5 |
| Anthracene | 90,7 | 9,3 |
| Fluoranthene | 87,3 | 12,7 |
| Pyrene | 87,1 | 12,9 |

# 'Raw' gas: IPA and DCM-bottles in series – effect of sampling flow-rate

- Conditions:
  - Filtered "raw" biomass gasification gas (ca. 5 $g/m^3_n$ of tars)
  - Tars were first trapped in isopropanol and the effluent gas was further sampled in dichloromethane
  - Gas flow rate **3 $dm^3_n$/min**
- Observations:
  - All tars dissolved completely in isopropanol

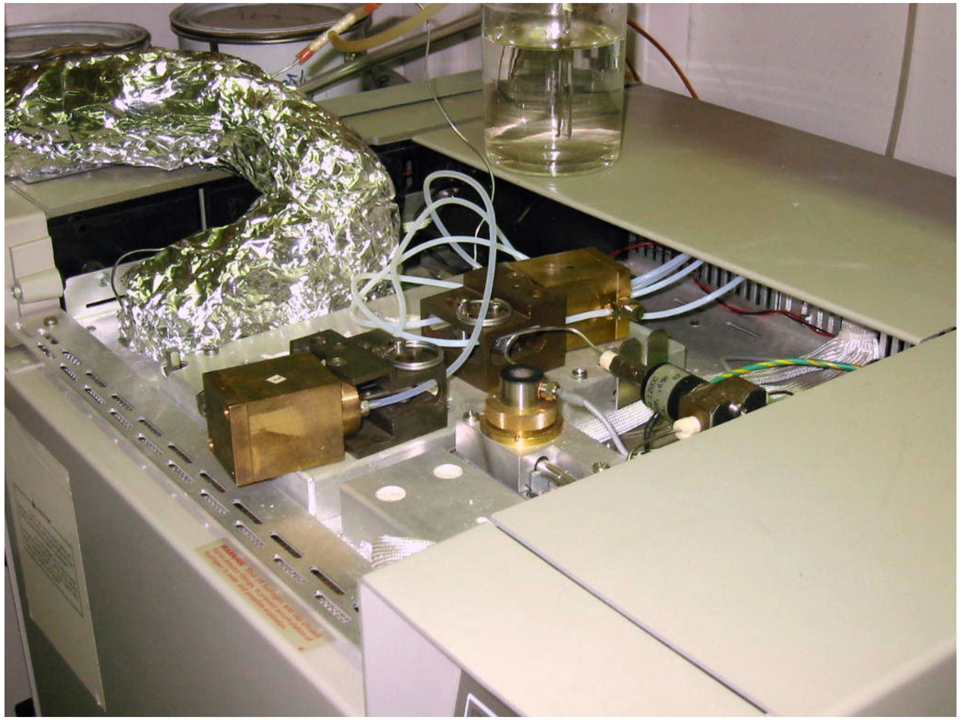
| Compound | 6 $dm^3_n$/min: Distribution in solvents, w-% | | 3 $dm^3_n$/min: Distribution in solvents, w-% | |
|---|---|---|---|---|
| | IPA | DMC | IPA | DMC |
| Benzene | 100,0 | 0,0 | 100,0 | 0,0 |
| Toluene | 100,0 | 0,0 | 100,0 | 0,0 |
| Styrene | 100,0 | 0,0 | 100,0 | 0,0 |
| Indene | 100,0 | 0,0 | 100,0 | 0,0 |
| Naphthalene | 99,9 | 0,1 | 99,9 | 0,1 |
| 2-Methyl-1-Naphthol | 85,6 | 14,4 | 99,0 | 1,0 |
| Phenanthrene | 90,5 | 9,5 | 100 | 0,0 |
| Anthracene | 90,7 | 9,3 | 98,9 | 1,1 |
| Fluoranthene | 87,3 | 12,7 | 99,0 | 1,0 |
| Pyrene | 87,1 | 12,9 | 98,9 | 1,1 |

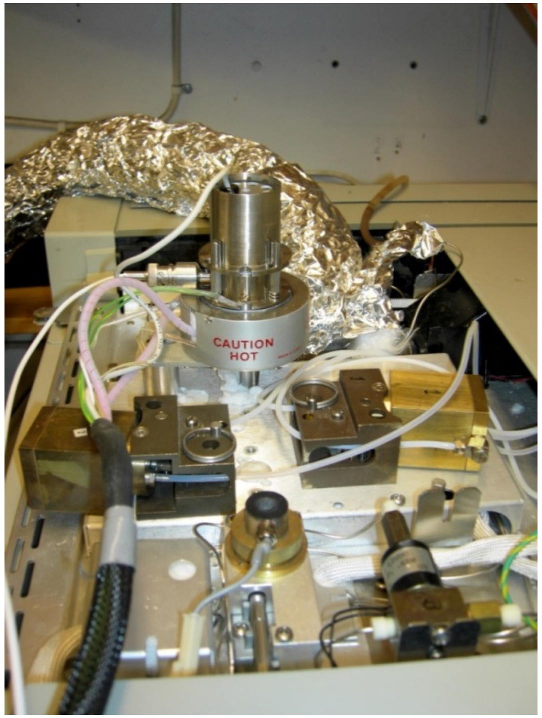
# "If anything can go wrong, it will" – despite VTT's 30 year's experience in tar sampling at least these things needed attention

- Transfer of knowledge from experienced staff to to younger people had not been sufficient enough
  - New technicians were not properly trained
  - Technical staff is working in three shifts during campaigns
    - Exchange of experiences is limited
  - Written instructions were not always clear
    - Every technician had a slightly different way of carrying out the sampling
- Glassware was not always cleaned well enough
  - Better instructions had to be given
  - Always use different glassware for raw and reformed gas
- The grease (in spray cans) used for ground joints was suddenly changed
- The flow rate during sampling of 'dirty' gas may have been too high
  - Should more precise instructions be included in the standard ?
- One batch of isopropanol contained remarkable amounts of toluene
  - All new batches of solvent must be analyzed
- Mistake in the laboratory when calculating GC-results

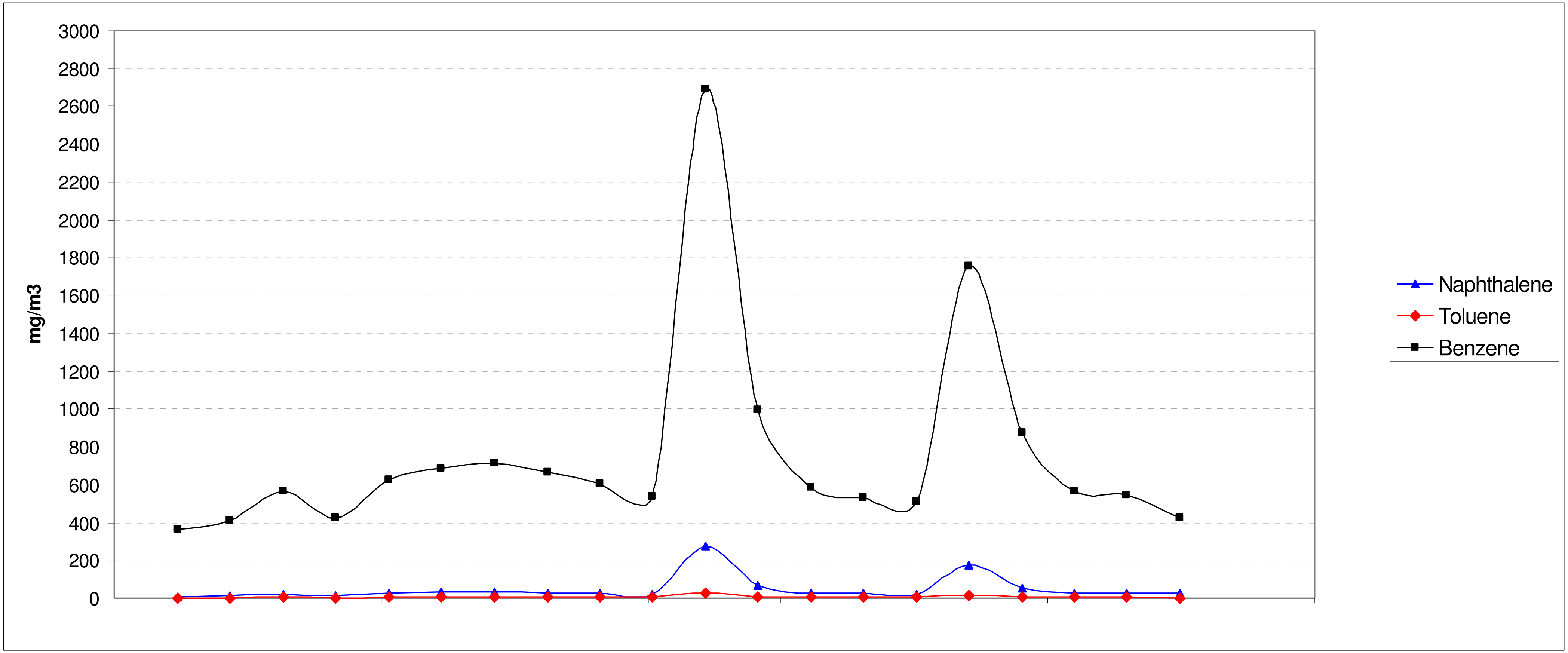
# On-line tar measurement method

- VTT started developing a new on-line tar measurement method for reformed biomass gasification gas about 10 Years ago and it has been in use for more than 5 Years
- The results were not always fully consistent with those obtained according to tar Protocol
  - What was the reason for this discrepancy ?
  - It turned out that the process was fluctuating and tar protocol is an averaging technique
  - Later a stable ”tar-generator” was developed





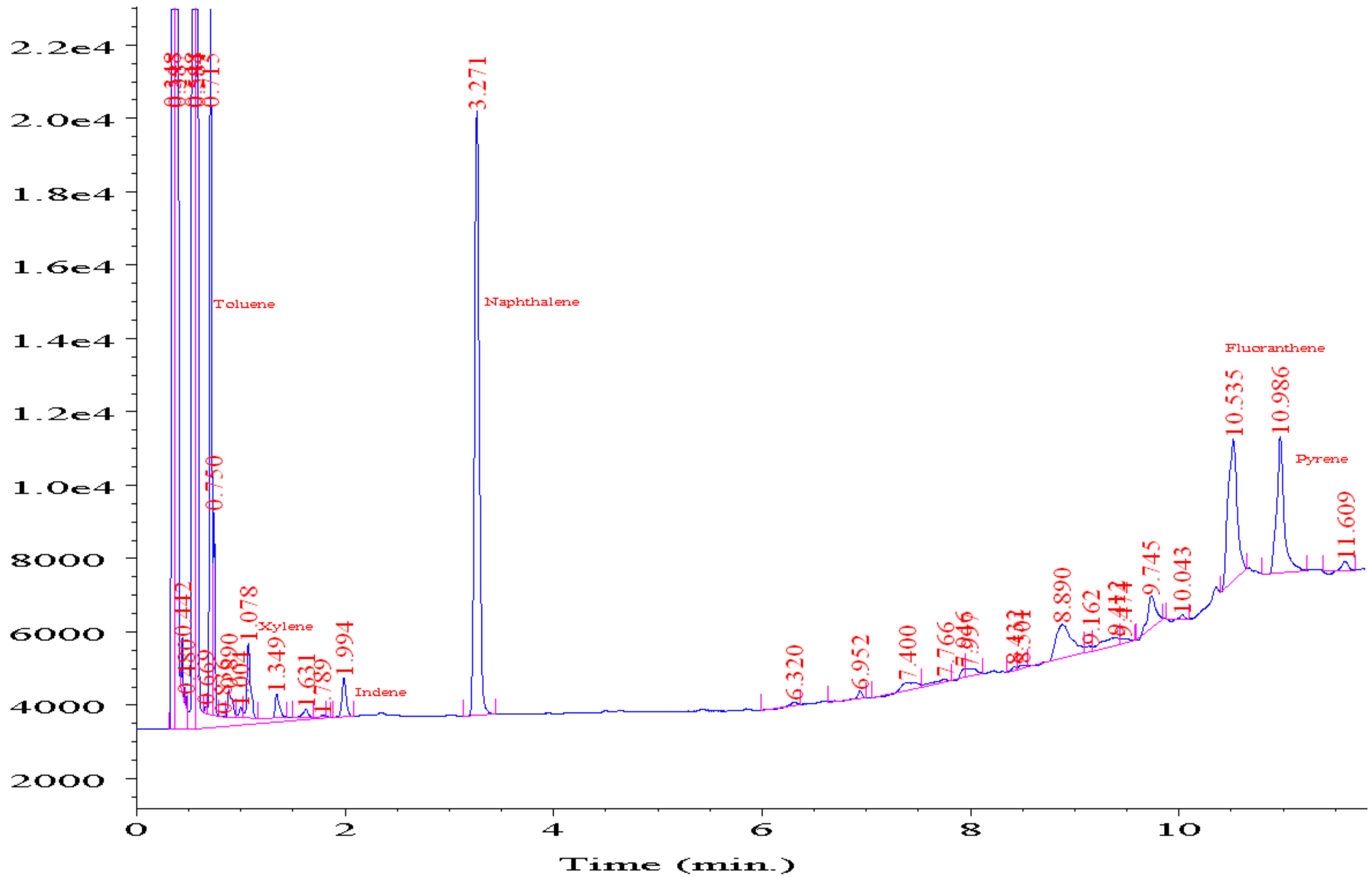
# Example of rapid tar measurement by on-line-GC




Results from EU BiGPower-project:
air-blown CFB gasification followed by tar reformer

# 'Rapid' on-line tar analysis

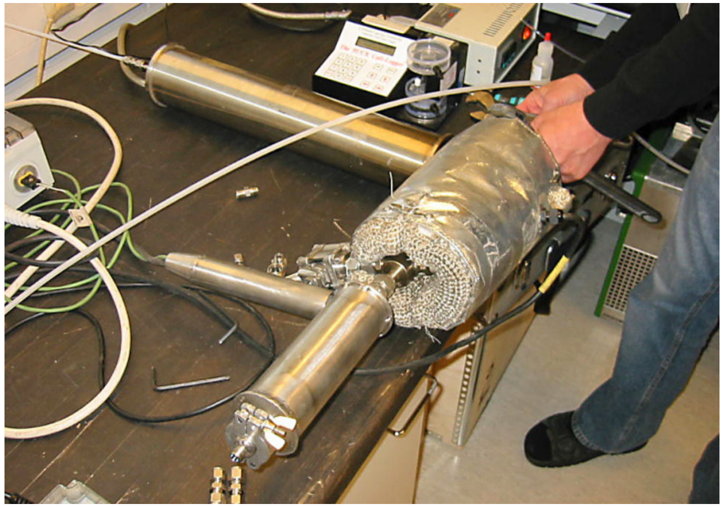
- Analysis time 5-20 min (several possible operation modes)
- Calibrated compounds:
  - Benzene
  - Toluene
  - Naphthalene
  - Phenanthrene
  - Anthracene
  - Fluoranthene
  - Pyrene
  - (if desired, 20 additional compounds)
- HP-1 (10 m x 0.53 mm x 0.26 µm) or HP Ultra 2 –column (25 m x 0.32 mm x 0.52 µm)
- Gas phase samples online
- Can be connected to the reactor automation system



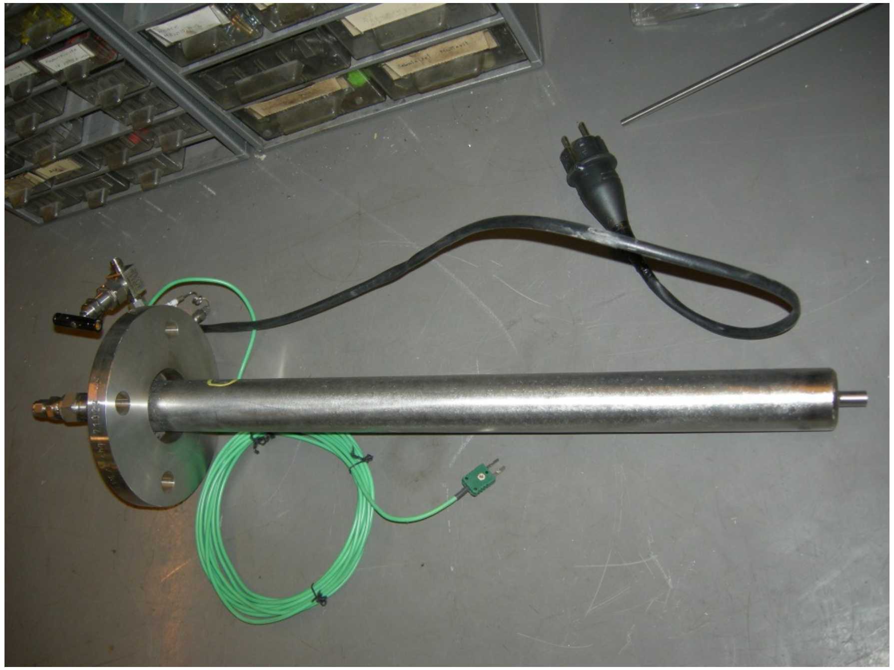
# Dilution sampling

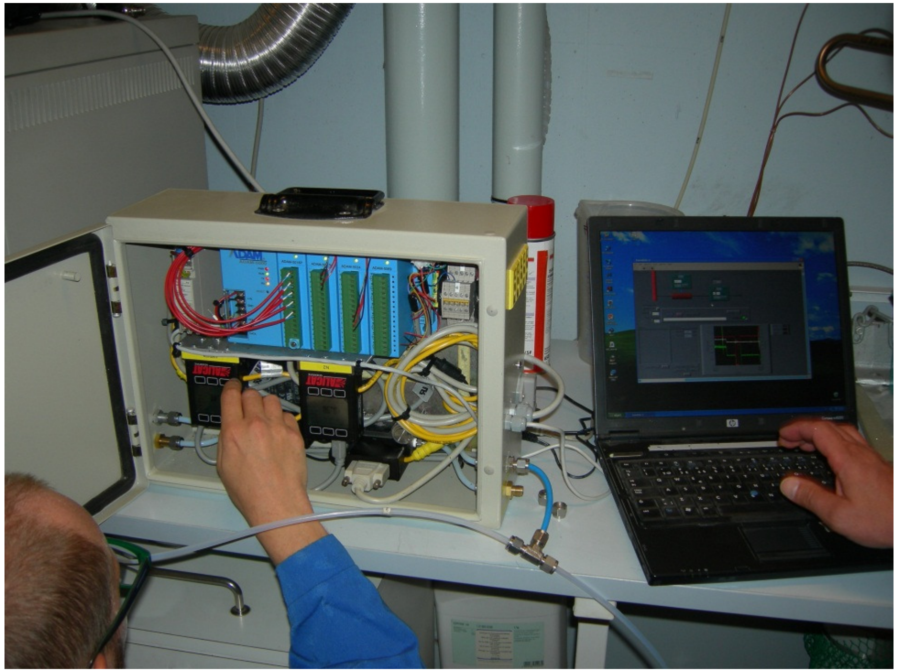
- Based on technology patented by VTT (e.g. US 8302495, FI 119450, WO/2007/080221)
- Can be applied to both atmospheric and pressurised systems
- Temperature range 280-800 °C
- Dilution ratio typically 0-100

- Preliminary results with very tarry raw gas have been promising
  - Results consistent with controlled off-line sampling
  - No problem with condensation of tars in the sampling lines
  - Good repeatability



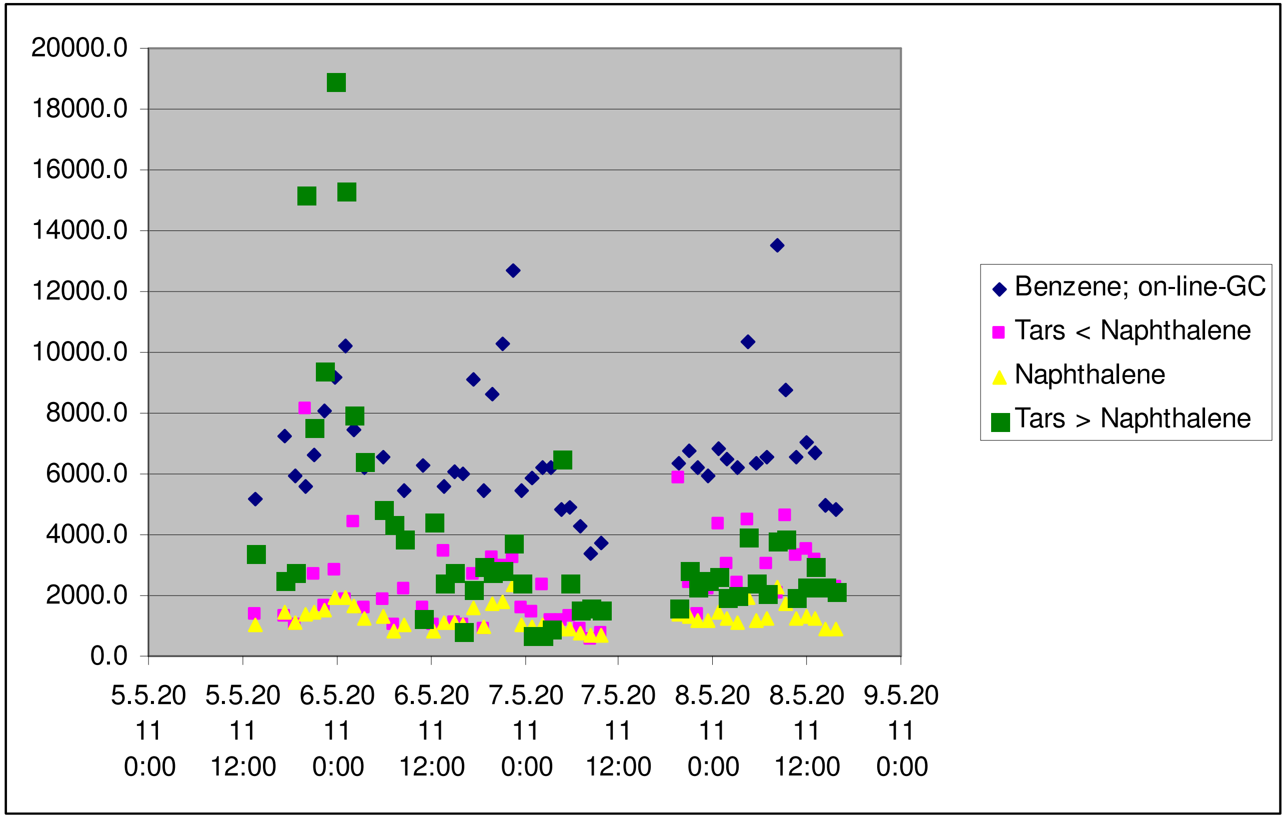
# Dilution sampling probe with control unit





# Dilution sampling: tar measurement of tarry gas

| | |
|---|---|
| Benzene | Acenaphtylene |
| Pyridine | Acenaphthene |
| Toluene | Dibenzofurane |
| Ethenylbenzene | Bibenzyl |
| m-Xylene | Fluorene |
| Ethynylbenzene | Phenanthere |
| Styrene | Anthracene |
| o-Xylene | Carbazole |
| Benzaldehyde | 1-Phenylnaphthalene |
| Phenol | 2-Methylanthracene |
| Benzonitrile | 4H-Cyclopenta(def)Phenantherene |
| 4-Methylstyrene | Fluoranthene |
| Indene | Benz(e)acenaphthylene |
| o-Cresol | Pyrene |
| m+p-Cresol | Chrysene |
| Naphthalene | 1,2 Benzanthracene |
| Quinoline | 2,3 Benzanthracene |
| Isoquinoline | Benzo(b)fluorant |
| Quinatsoline | Benzo(e)pyrene |
| 1H-Indole | Benzo(a)pyrene |
| 2-Methylnaphthalene | Perylene |
| 1-Methylnaphthalene | Benzo(ghi)peryle |
| Biphenyl | Anthanthrene |
| 2-Ethylnaphthalene | Coronene |
| 1.6 Dimethylnaphtalene | |



# Comparison of tar analyses by on-line (dilution) and of-line methods

| mg/m³n | On-line | Off-line |
|---|---|---|
| Benzene | 10101.1 | 12724.7 |
| Toluene | 689.5 | 689.5 |
| m-Xylene | 41.0 | 32.5 |
| Styrene | 128.0 | 144.5 |
| o-Xylene | 0.0 | 0.0 |
| Phenol | 38.0 | 40.0 |
| Indene | 395.9 | 374.0 |
| Naphthalene | 3792.4 | 3024.7 |
| 2-Methylnaphthalene | 58.0 | 66.9 |
| 1-Methylnaphthalene | 46.5 | 36.3 |
| Biphenyl | 86.3 | 68.4 |
| 1.6 Dimethylnaphtalene | 0.0 | 2.7 |
| Acenaphtylene | 468.7 | 490.6 |
| Dibenzofurane | 65.0 | 71.5 |
| Fluorene | 174.8 | 174.6 |
| Phenanthere | 638.0 | 602.4 |
| Anthracene | 189.4 | 157.3 |
| 4H-cyclopental(def)Phenanthrene | 79.8 | 52.2 |
| Fluoranthene | 501.2 | 252.2 |
| Pyrene | 391.0 | 229.6 |

a) Laboratory gasifier

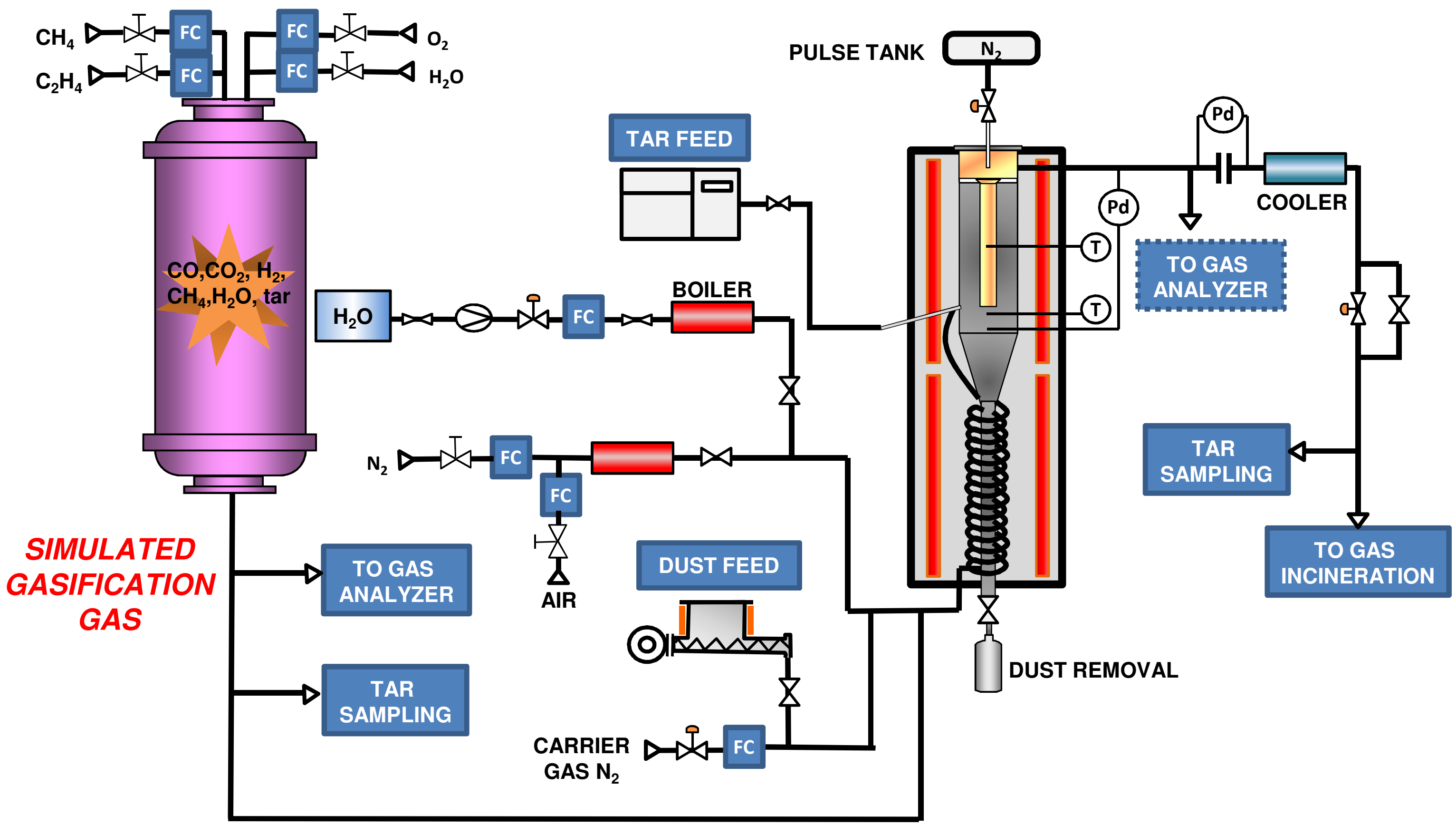
| mg/m³n | On-line | Off-line |
|---|---|---|
| Benzene | 6630,2 | 7380,1 |
| Pyridine | 45,1 | 83,8 |
| Toluene | 866,6 | 674,4 |
| m-Xylene | 82,4 | 30,8 |
| Styrene | 238,8 | 196,6 |
| Phenol | 927,9 | 702,1 |
| 4-Methylstyrene | 146,5 | 114,5 |
| Indene | 233,9 | 252,7 |
| Naphthalene | 1449,9 | 1702,2 |
| 2-Methylnaphthalene | 101,9 | 72,3 |
| 1-Methylnaphthalene | 55,5 | 38,7 |
| Biphenyl | 93,5 | 85,5 |
| 1.6 Dimethylnaphtalene | 31,6 | 0,0 |
| Acenaphtylene | 334,8 | 339,7 |
| Acenaphthene | 18,0 | 20,6 |
| Dibenzofurane | 163,2 | 175,4 |
| Fluorene | 59,9 | 52,9 |
| Phenanthere | 832,5 | 291,6 |
| Anthracene | 178,4 | 56,2 |
| Fluoranthene | 814,0 | 131,1 |
| Pyrene | 717,8 | 78,7 |
| Chrysene | 243,1 | 14,8 |

b) Commercial gasifier

# Dilution sampling: tar and particle measurement from highly tar-laden gas

# Pressurised hot gas filtration test rig ALMA

- Simulated gasification gas including soot and tars is fed to a filter unit.
- Pressures up to 5 bar(g), filtration temperatures up to 850 °C

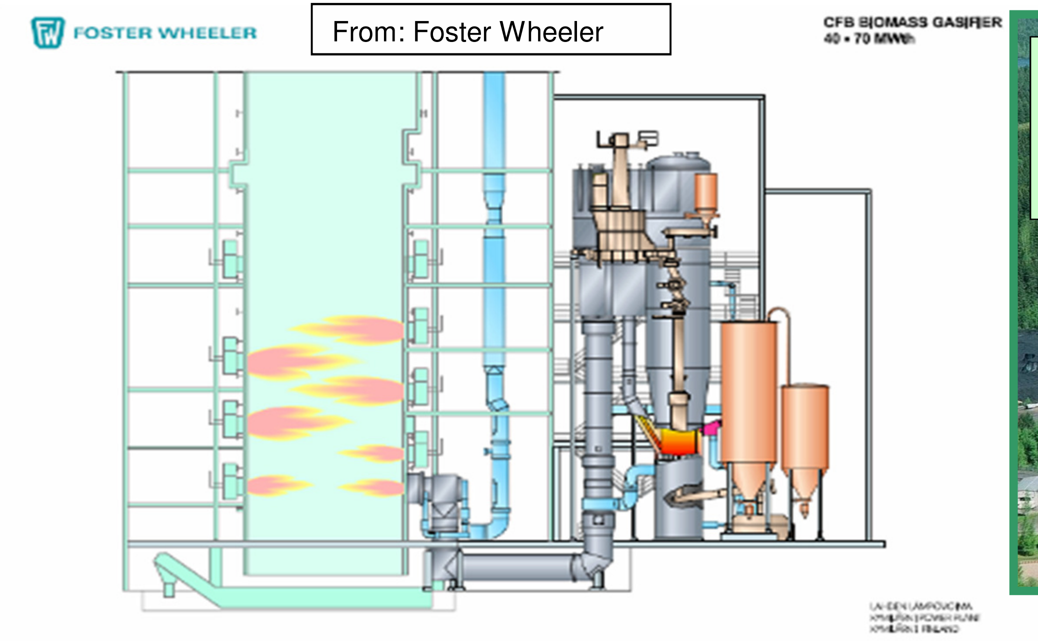


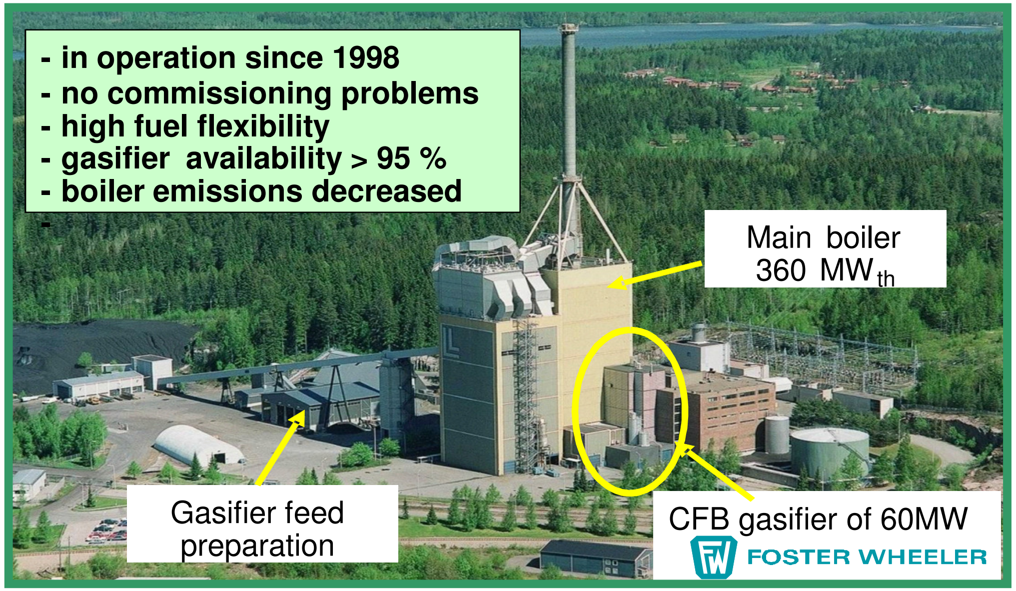

# Observations on tar measurements

- Under carefully controlled conditions, the Tar Protocol seems to be a reliable method for the analysis of tars **when the concentration of heavy tars is fairly low**
- However, there are several possible sources of error and care must be taken to avoid them
- As a typical off-line method the Protocol is fairly labour-intensive and time-consuming. A fast on-line tar analysis method for ‘clean gases’ overcomes this problem. With this method the concentration of typical light tar components can be analyzed in about 15 minutes
- **When the gas contains large amounts of heavy tars the Tar protocol may underestimate their amount (3-10 fold!).** With fairly clean gases the results of on-line measurement have been in good agreement with the results from controlled off-line analysis off the corresponding samples. On-line analysis has proved to be especially useful in transient conditions where the gas composition changes quickly
- Combined with dilution sampling, on-line method can be applied also to ’dirty’ gases

# Efficient utilisation of wastes and biomass residues in existing power plants

## a cost-effective way to reduce $CO_2$ emissions of power plants




**New CFB gasification plants are in commissioning/under construction**

- two new gasifiers (2x80 MW) at Lahti waste-to-energy plant (supplier: Metso)
- one large gasifier (140 MW) in Vaasa (supplier: Metso)
- lime kiln gasifier (48 MW) at Joutseno (supplier Andritz)
- lime kiln gasifier (12 MW) at Varkaus was returned to air-blown operation mode after succesfull $O_2$-blown test campaigns for Neste Oil and Stora Enso (Foster Wheeler)

From: Kari Salo, Andritz, 2011

# Metsä-Botnia, Joutseno gasification plant for lime kiln


CARBONA ANDRITZ

# 2G Biofuels Project and New RES-Infra

- VTT will move it's Gasification and Pyrolysis test equipment from Otaniemi to an industrial area in Kivenlahti, Espoo
- New pilot facilities will also be constructed
- Start-up at new site in Q3-Q4/2014, testing is continued in Otaniemi using present facilities until end 2013

2G Biofuels R&D&Piloting poject
7.2 M€: 2012-14, 2nd phase planned for 2015-16

VTT RES-Infra Investment Funding for equipment

# Pilot/PDU-scale Gasification Test facilities of VTT in 2014

## High-Pressure BFB gasification PDU (new test facility)

- Bubbling Fluidized-Bed gasification, fluidization by air/$O_2$/steam/recycle gas
- max. pressure 25 bar, thermal capacity max. 0.5 MW, gas flow rate ca. 200 m3n/h
- High-temperature filter, tar and methane reforming, gas cooling
- Slip stream or full stream testing of final gas clean-up and synthesis processes
- Continuous operation, typically 100-500 hour-long test campaigns

## Intermediate Pressure CFB gasification Pilot plant (existing test rig)

- Pressure 2-6 bar, fuel capacity max. 0.5 MW, gas flow rate 200 m3n/h
- CFB-gasifier, fluidization by air/$O_2$/steam/recycle gas
- High-temperature filter, tar and methane reforming, gas cooling
- Slip stream or full stream testing of final gas clean-up and synthesis processes
- 1-2 week long test campaigns

## Low-Pressure CFB gasification Pilot plant (present plant modified)

- Fuel capacity max. 300 kW
- Air gasification with single gasifier reactor (mainly waste gasification)
- Dual-Bed steam gasification (smaller size syngas applications 50 .. 150 MW)
- High-temperature filter, tar and methane reforming, gas cooling

## Bench-scale and laboratory testing facilities

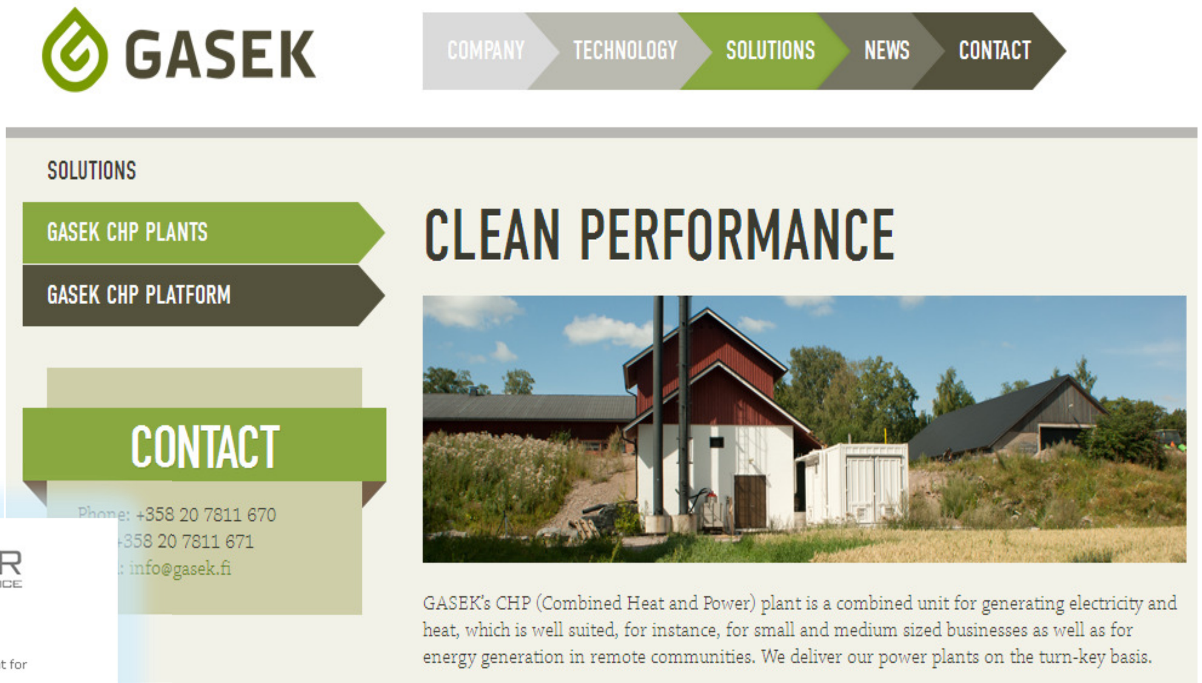
- Atmospheric-pressure BFB and CFB gasifiers with hot filtration
- Pressurized BFB gasification reactor
- Pressurized filtration and reforming test facilities (operation with slip streams or with synthetic gas)
- Catalytic conversion R&D laboratory, Fuel reactivity and ash sintering R&D laboratory

# Gasification based small scale CHP development in Finland

- Downdraft gasifier followed by gas purification and gas engine
- Dried wood chips as fuel

## Gasek

- Power output 50 kW, heat output 100kW
- R&D site in Reisjärvi
- Contact: info@gasek.fi





## Volter

- Power output 30 kW, heat output 80 kW
- Three plants in Oulu region
- Contact: jarno.haapakoski@volter.fi

Sources: www.gasek.fi, www.volter.fi

# Gasification and filtration experiments with AFB60

- The main focus of experiments:
  - Performance of the filter at temperatures 550-800 ℃ (filter blinding issues etc.)
  - Alkali metal retention on the filter: alkali metal measurements after filter
  - Bed sintering
  - Filter ashes will be analysed in a more detail
- Experiments will be carried out with an atmospheric pressure, bench-scale gasification test rig AFB60:
  - Bubbling fluidised-bed gasifier (bed i.d. 63 mm)
  - Hot gas filter equipped with 2-3 rigid ceramic filter candles: SiC, o.d. 60 mm