Supplementary tools for gasification gas analysis

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Matti Reinikainen, Noora Kaisalo, Sanna Tuomi, Pekka Simell
VTT Technical Research Centre of Finland

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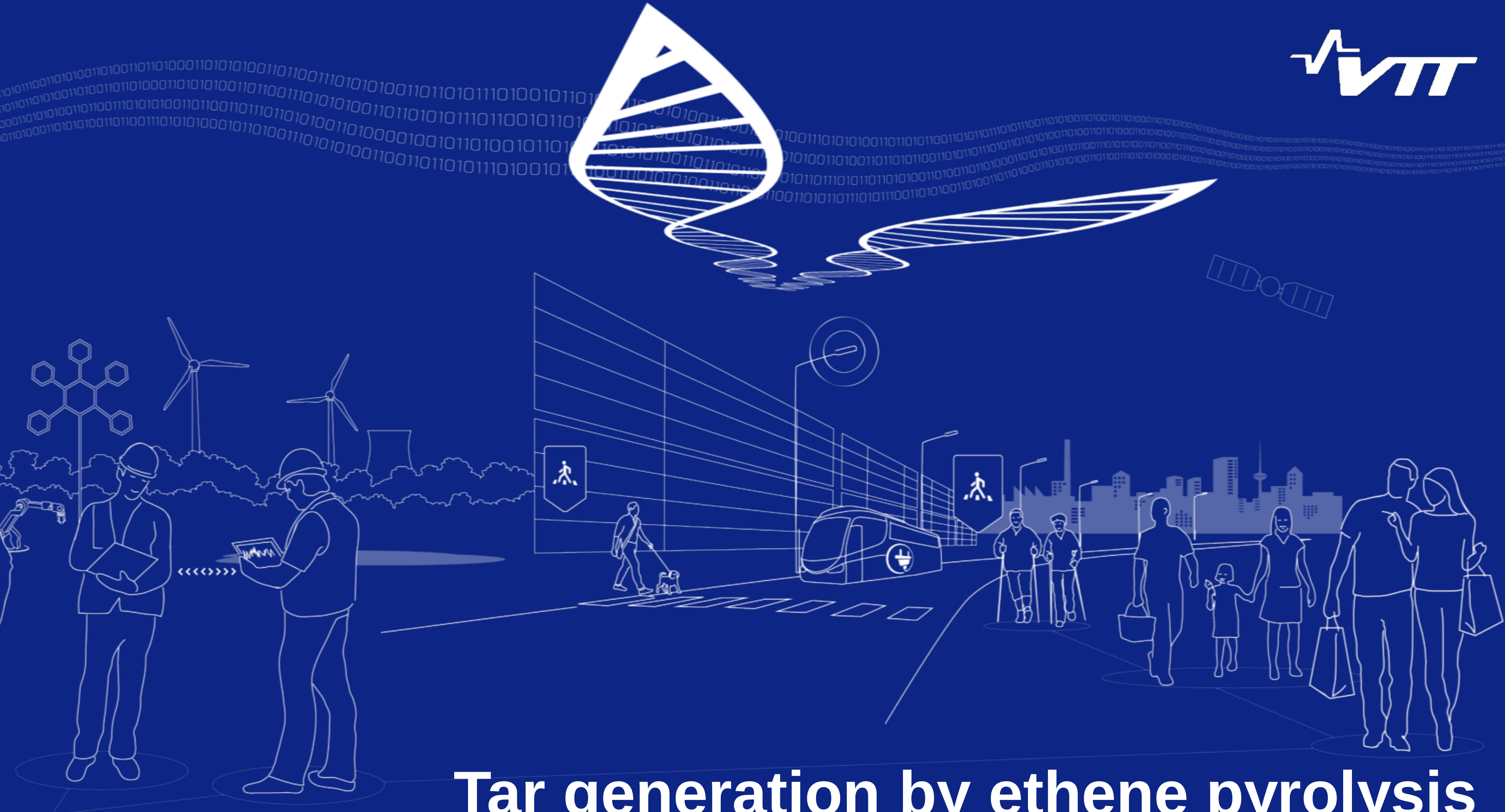


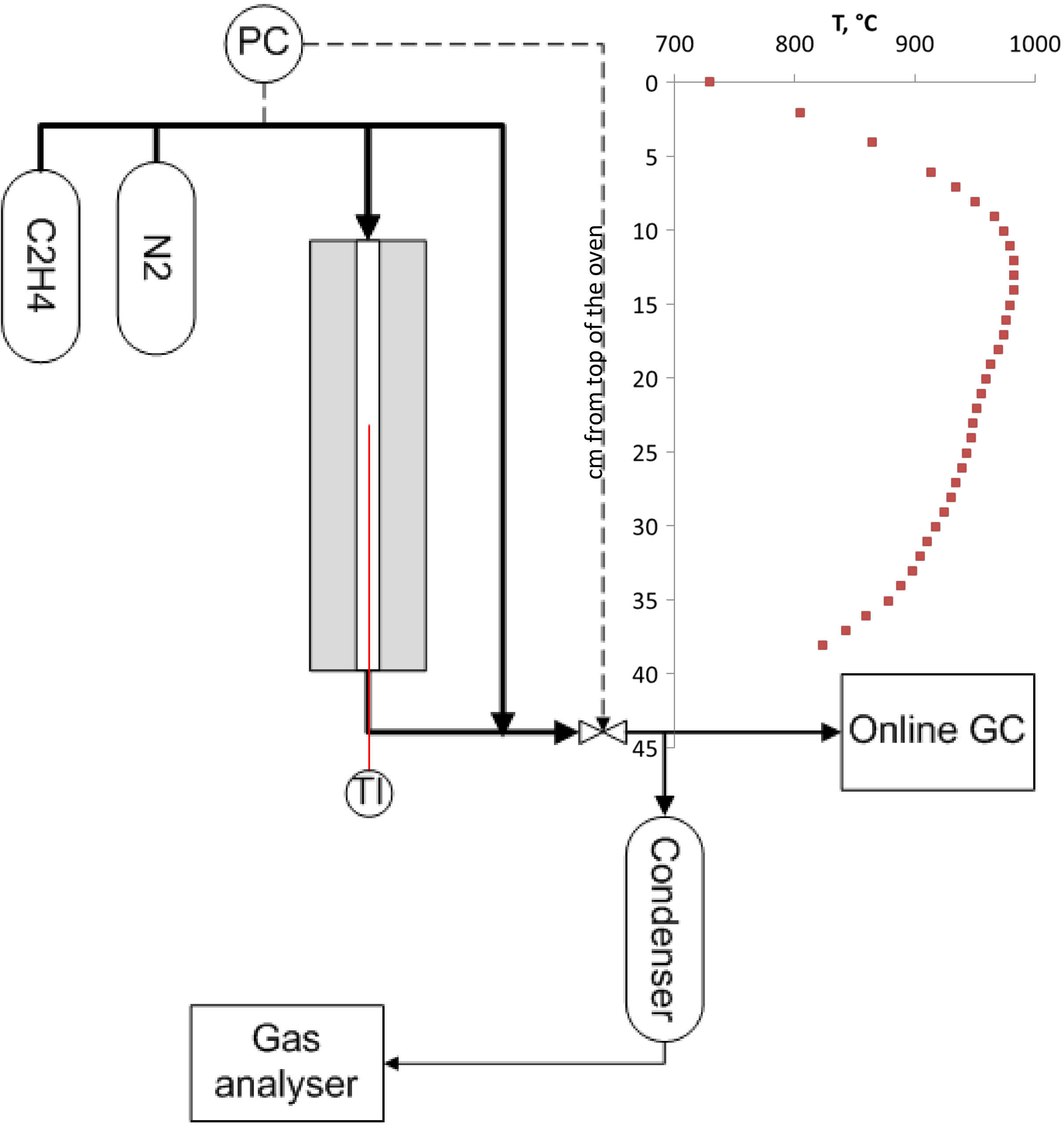
Tar generation by ethene pyrolysis

Background

- The objective was to generate a complex tar mixture that could be used for gas cleaning studies in lab and bench-scale.
- The concept of ethene pyrolysis in tar generation was **first tested in lab-scale** in varying conditions.
- The **next step was to combine the production of the main gasification gas compounds and tar generation**. This was carried out in HOTPURI reactor by steam reforming/partial oxidation of natural gas and simultaneous ethene pyrolysis. Natural gas, ethene, steam and oxygen were used as feed gases. The produced gas contains the main gasification gas compounds, a mixture of tars resembling real biomass gasification-based tar and also soot.
- HOTPURI reactor has been used in 2013/2014 to produce realistic gasification gas to a bench-scale hot gas filter test rig.
  - More economical solution compared to the use of cylinder gases in bench-scale testing

Ethene pyrolysis experiments in lab-scale

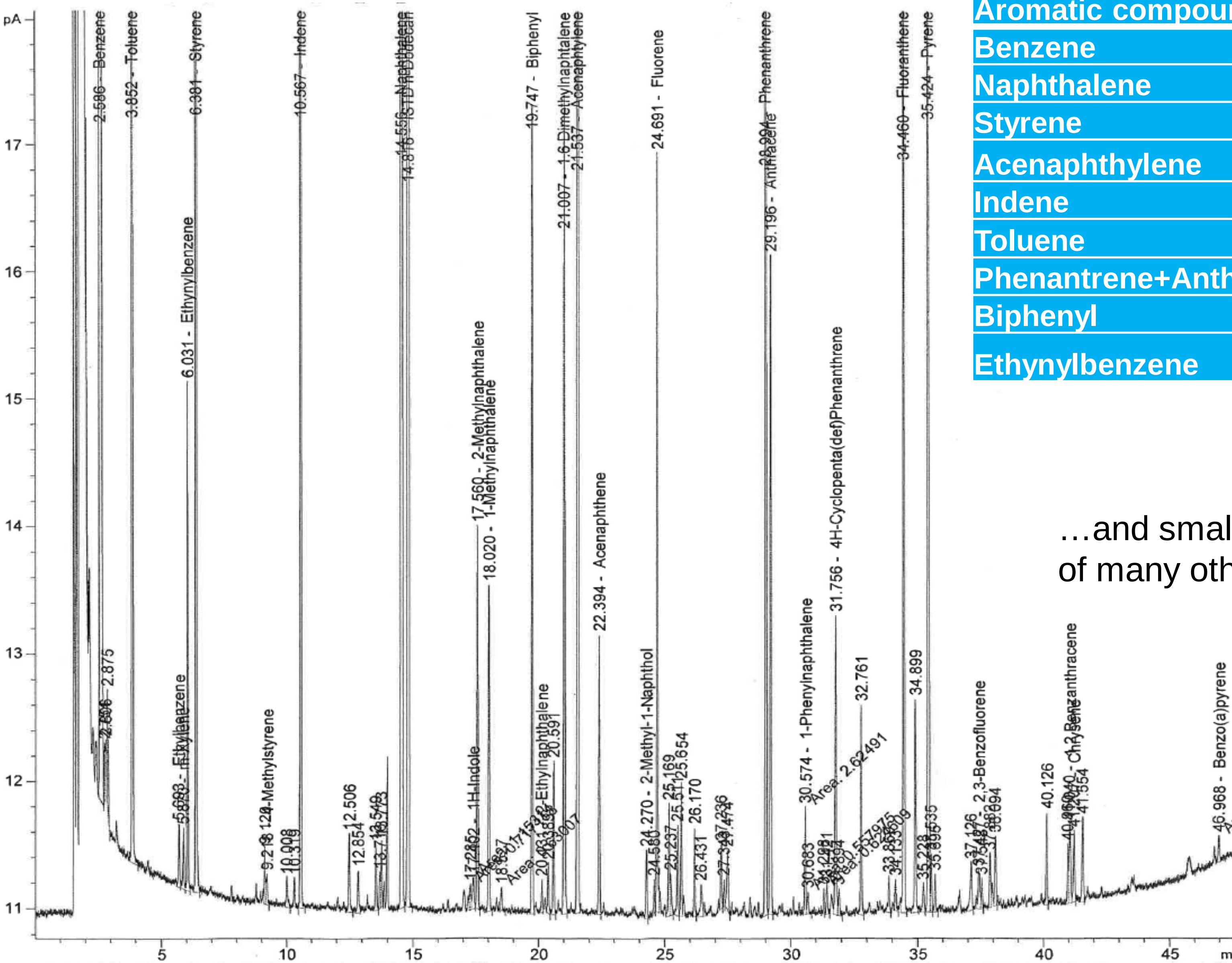
Laboratory set-up and conditions



- Feed: 50 000 vol-ppm ethene in nitrogen
- Conditions tested
  - Pressure: 1-6 bar(a)
  - Temperature: 800 – 975 °C
  - Residence time: 0.09-3.34 s (calculated for the whole reactor length)

Example of most abundant tar compounds

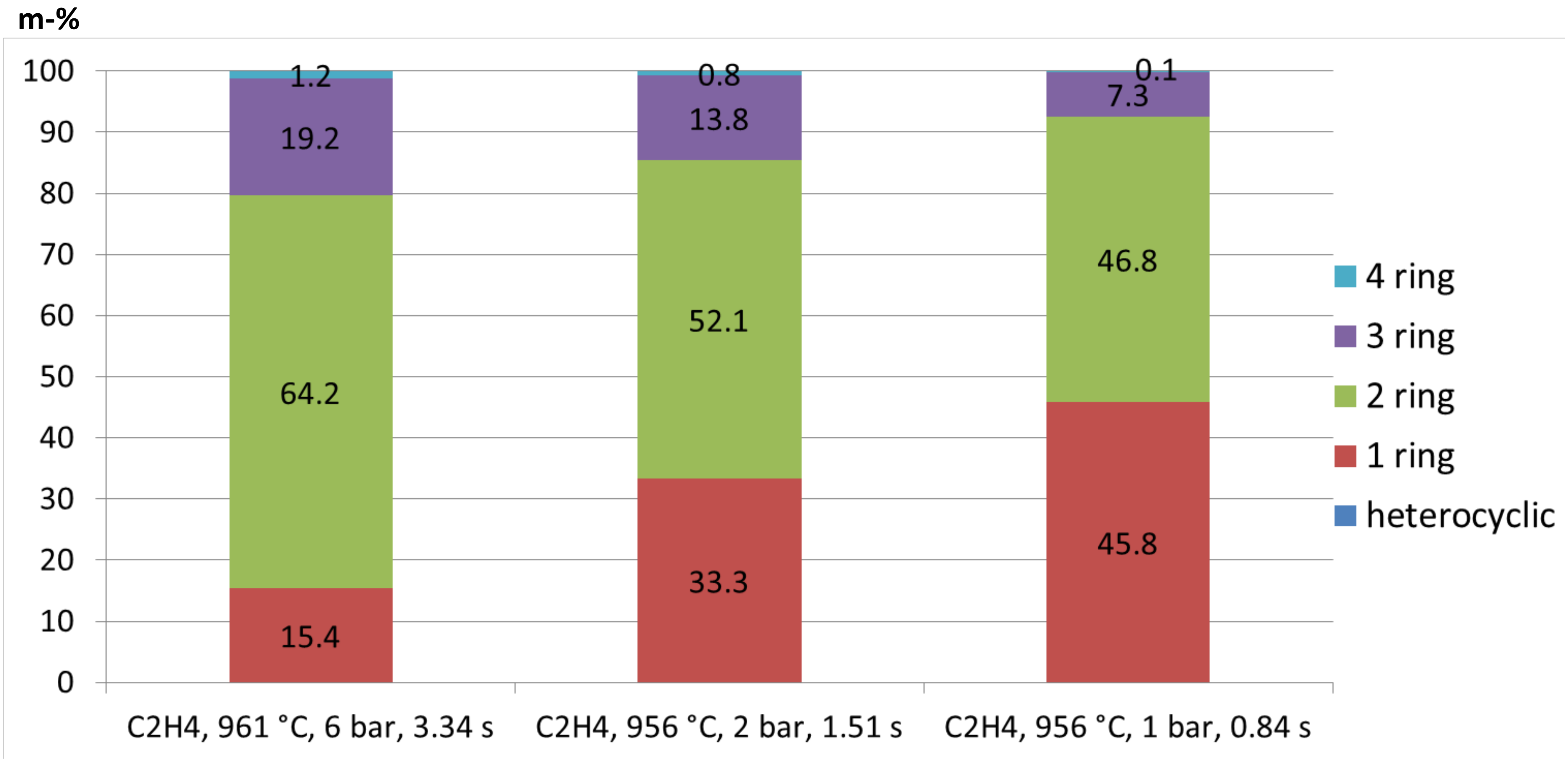
C_2H_4, 961 °C, 6 bar, 3.34 s



Aromatic compound	Amount, ppm
Benzene	2362
Naphthalene	535
Styrene	129
Acenaphthylene	91
Indene	60
Toluene	42
Phenantrene+Anthracene	29
Biphenyl	19
Ethynylbenzene	18

…and smaller amounts of many other compounds

Tar composition from ethene pyrolysis



Benzene mg/m3	8236	4194	1510
Total tar mg/m3	5713	3126	828

Examples of the formation of light hydrocarbons

	C_2H_4, 961 °C, 6 bar, 3.34 s	C_2H_4, 956 °C, 2 bar, 1.51 s	C_2H_4, 956 °C, 1 bar, 0.84 s
H2, vol-%	2.9	1.4	0.7
CH4, ppm	9769	2449	838
Ethene, ppm	10590	27122	36192
Acetylene, ppm	1530	6877	5554
C3, ppm	77	151	145
C4, ppm	118	411	443
C5, ppm	84	377	329
C6, ppm	1	6	6

- Ethene conversion remarkable only above 950°C
  - At 905 °C the conversion was 1.2% (1 bar, 0.6 s)
  - At 951 °C the conversion was 16.1% (1 bar, 0.6 s)

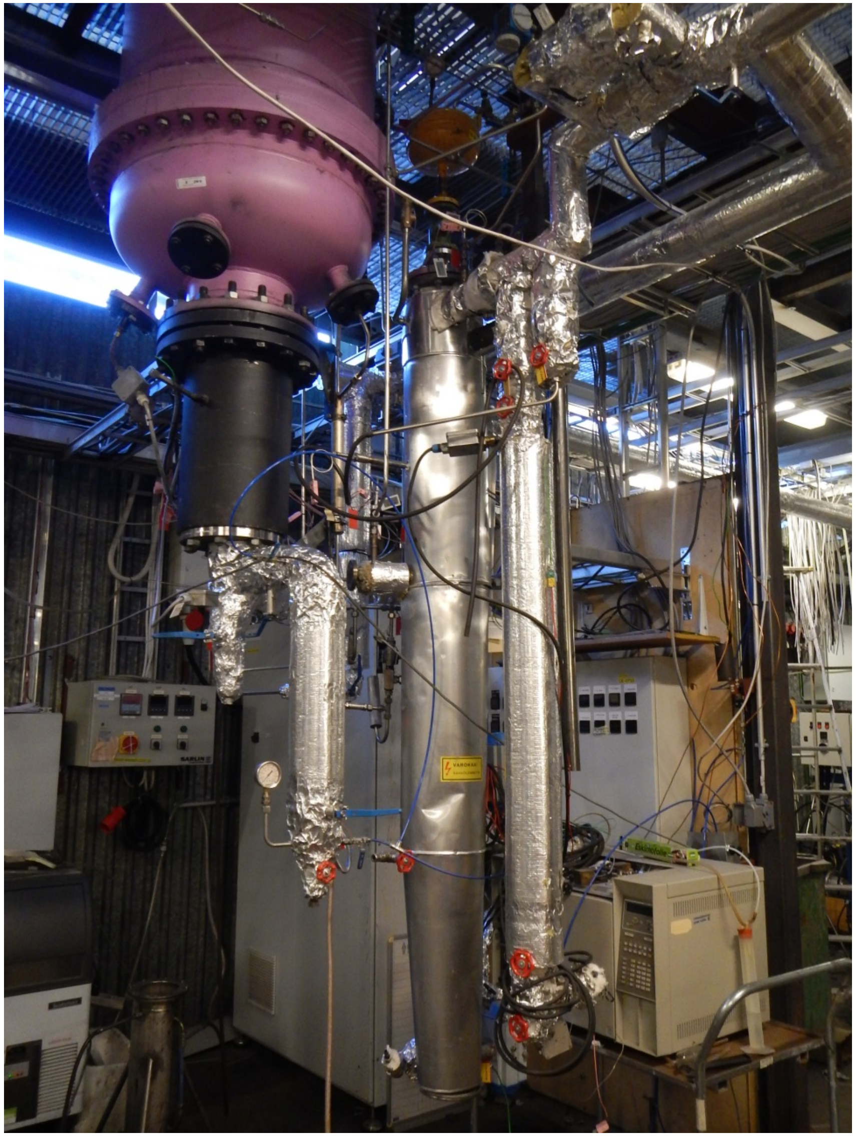
Generation of realistic tar-laden gasification gas in the 'HOTPURI'-reactor

Realistic tar-laden gasification gas in HOTPURI reactor

- Operation principle
  - Simultaneous production of main gasification gas components and tars from natural gas, ethene, oxygen and steam
  - Steam reforming/partial oxidation of natural gas and ethene pyrolysis

- HOTPURI reactor
  - Max. pressure 10 bar(a) and temperature 1200 °C
  - Electrically heated
  - Feed gases: natural gas, oxygen, steam and ethene
  - Gas composition measured after the reactor:
    1. Continuous gas analyzer for measuring CO, CO2, H2, CH4
    2. Gas bag samples: analyzed with GC for the main gasification gas components and C2-C5 hydrocarbons
    3. Tar sampling according to the Tar Protocol as well as
    4. **on-line tar measurement (dilution sampling)**

HOTPURI-reactor

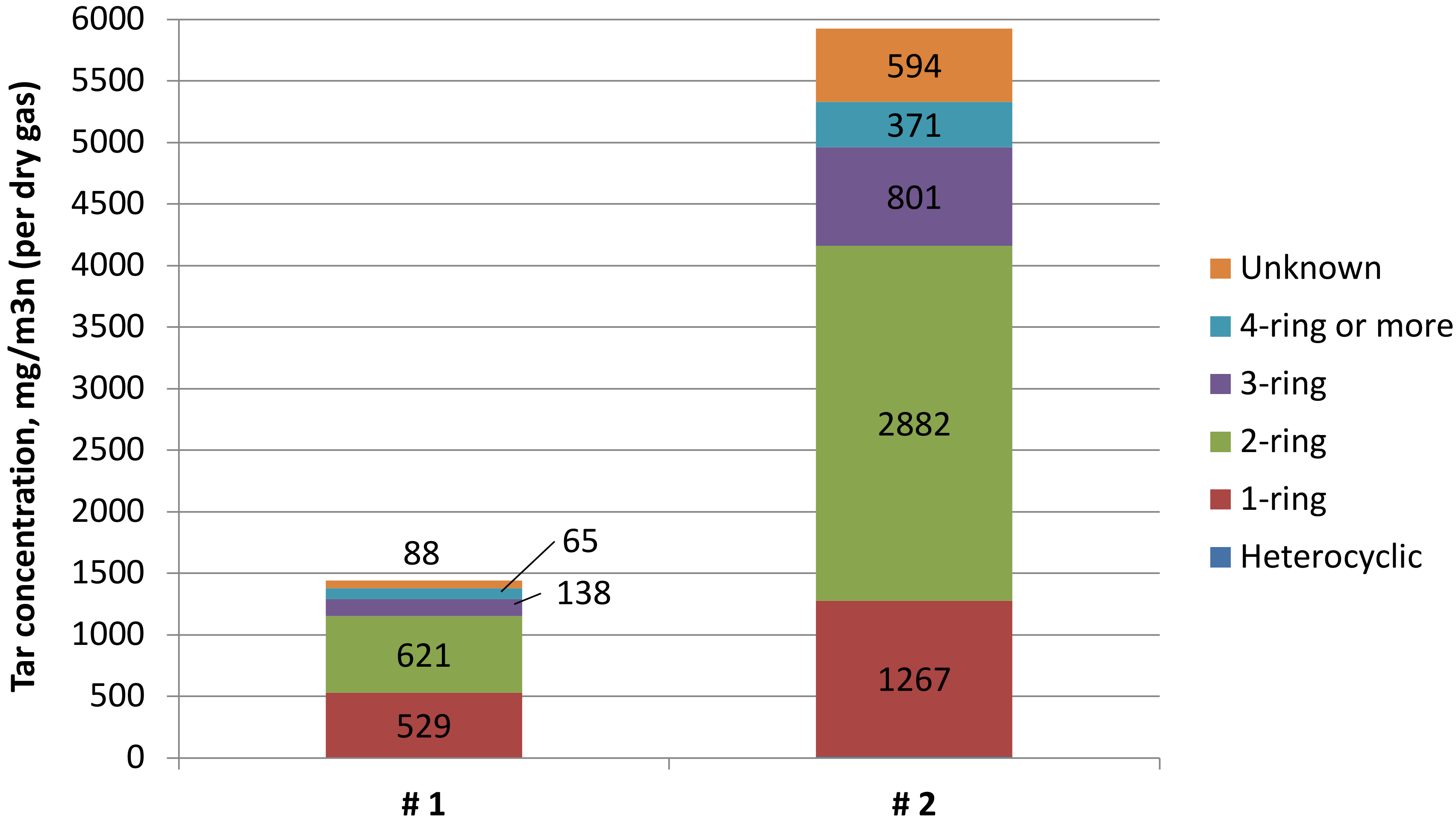


Examples of gas and tar composition

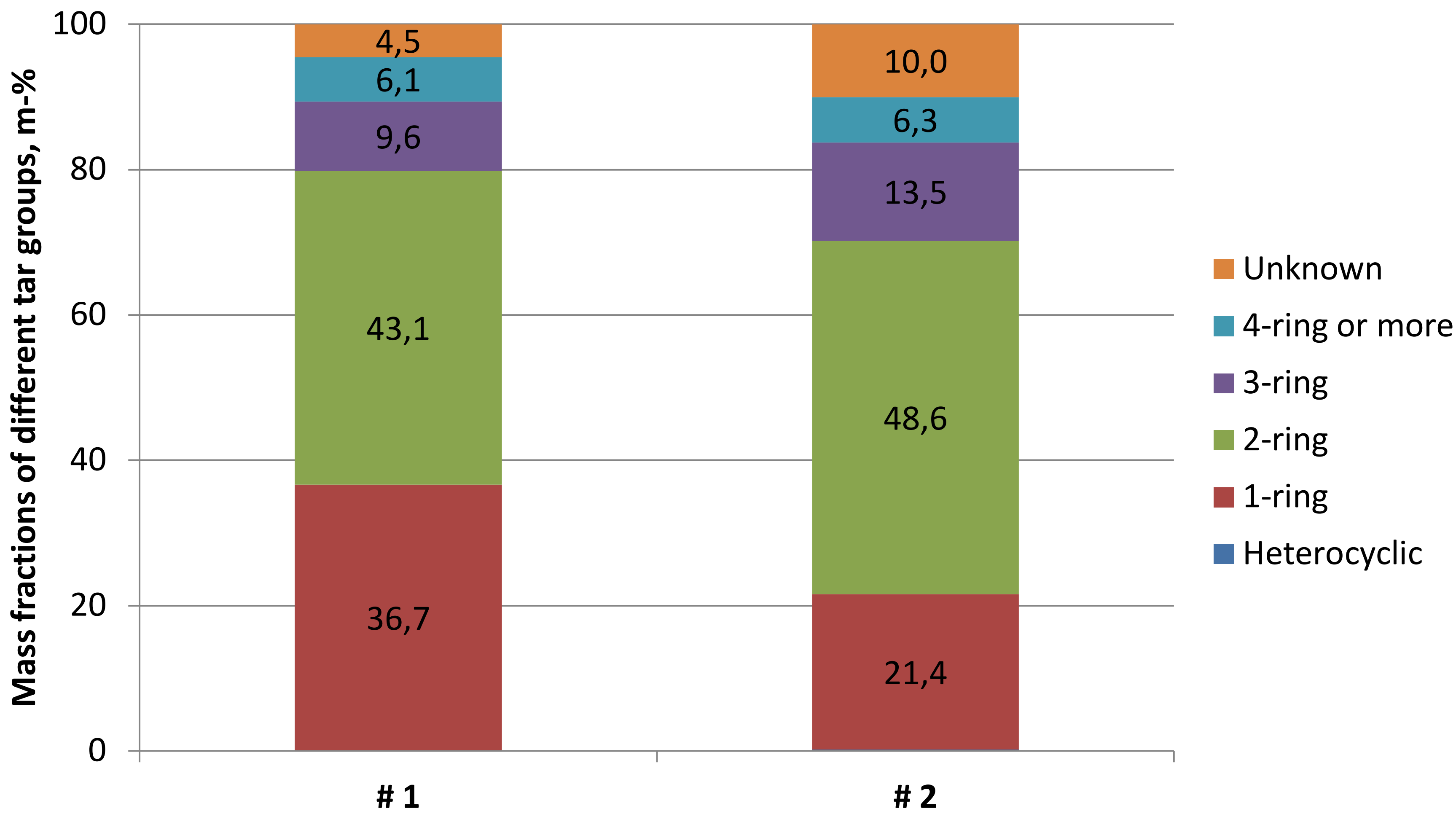
- The produced gas contained in excess of methane as the reactions conditions and feed gas ratios were not tuned for efficient conversion of natural gas. The tar yield was more important for our purposes.
- In addition to the main gas compounds, benzene and tars, also soot was formed.

TEST	# 1	# 2
Max temp in reactor, °C (appr.)	960	1100
Pressure	atmospheric	atmospheric
Residence time, s	> 3	> 4
FEED GAS COMP.	**m-%**	**m-%**
CH_4	28,9	24,5
C_2H_4	10,4	21,1
O_2	22,7	18,1
H_2O	38,0	36,4
PRODUCT GAS COMP. (dry basis)	**vol-%**	**vol-%**
CO	13,9	18,9
CO_2	12,7	8,6
H_2	30,8	44,0
CH_4	***36,7***	***24,6***
C_2H_2	0,1	0,1
C_2H_4	5,4	3,6
C_2H_6	0,29	0,19
C3-C5Hx	0,09	0,03
H_2O, vol-%	43,0	31,1
Total tar, g/m3n (per dry gas)	***1,4***	***5,9***
Benzene, g/m3n (per dry gas)	***3,7***	***15,0***

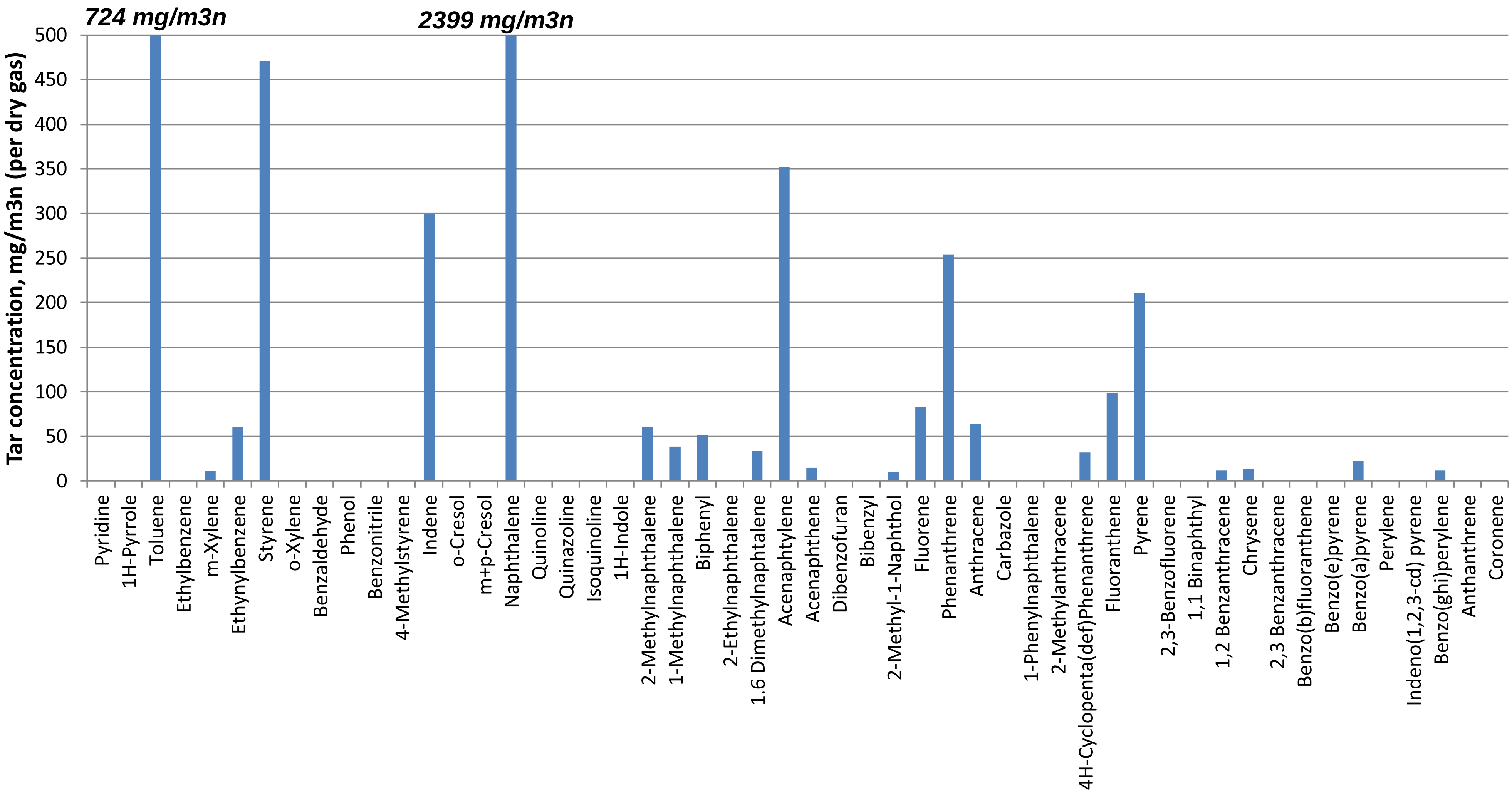
Examples of tar (excl. benzene) composition (1)



Examples of tar composition (2)



Examples of tar composition (3)
- Tar compounds in test # 2

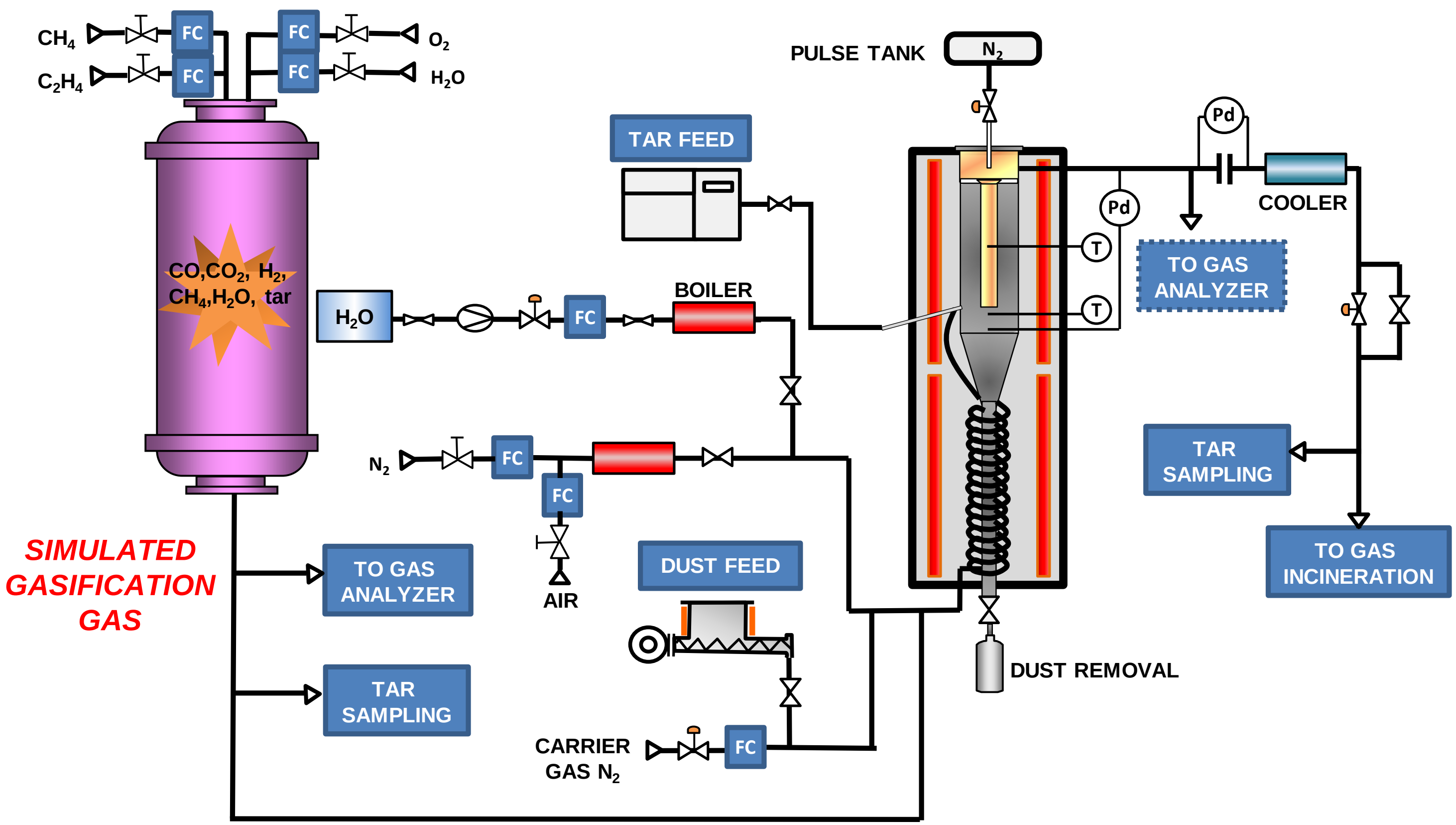


Experiences and remarks on tar generation by ethene pyrolysis

- Efficient conversion of ethene to tars requires high temperatures, preferably temperatures above 950 °C.
- Increase in temperature, pressure and residence time increases the tar yield.
- Soot is formed as a side product in ethene pyrolysis. Soot and heavy tar compounds cause fouling and plugging of the system and analysis lines.
- Tar production by ethene pyrolysis is sensitive to changes in the reaction conditions and therefore stable conditions must be maintained in the reactor to ensure steady tar levels over time. **However, this can be done**. Furthermore, tar concentration should preferably be monitored by online or at least semi-continuous methods.
- Gas and tar composition can be adjusted by changing the reaction conditions and feed gas ratios. However, it may be quite challenging e.g. to obtain a similar gas composition at different pressure levels.

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



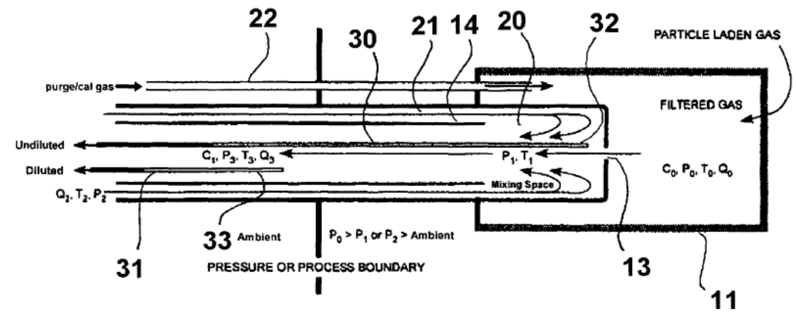
Dilution sampling

Dilution sampling

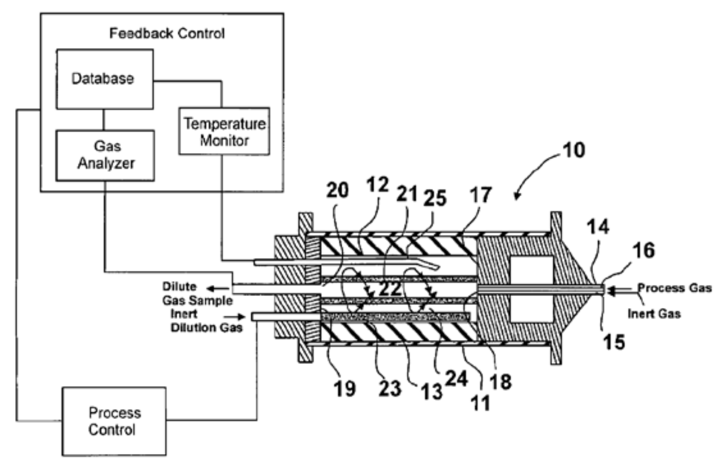
- Avoid condensation and change in gas composition during sampling
- Makes it possible to use a wide range of detectors – also online
- Can be used in very high temperature and dirty environments for on-line monitoring of tars, alkali metals, halogen compounds, ammonia, sulphur, heavy metals and particles
- In many applications on-line dilution sampling can pioneering technique, for instance:
  - Diluted sampling probes are not available commercially
  - Reliable on-line tar measurements are not available on the market
  - On-line alkali measurements are not available
  - Possibility to build up a simultaneous multi-analysis systems for difficult gas streams
- It is very important that the sample is cooled and "extinguished" as fast as possible after taking from the process. The molecules and particles of a sample le steel pipe tend to change as the temperature drops and the gas is allowed to come into free contact with the gradually cooling walls of the pipe.

Dilution sampling probes

- Several designs found in literature, for instance:
  - US 7 712 834 (Felix et al.)



  - US 7631566 (Farthing et al.)



Dilution sampling probes (continued)

- US 7720361 (Felix et al.)

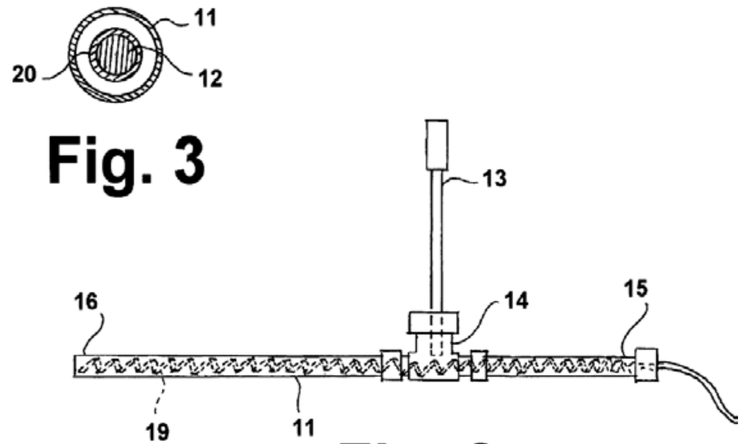


Fig. 2

- US 8302495 (Vesala, VTT)

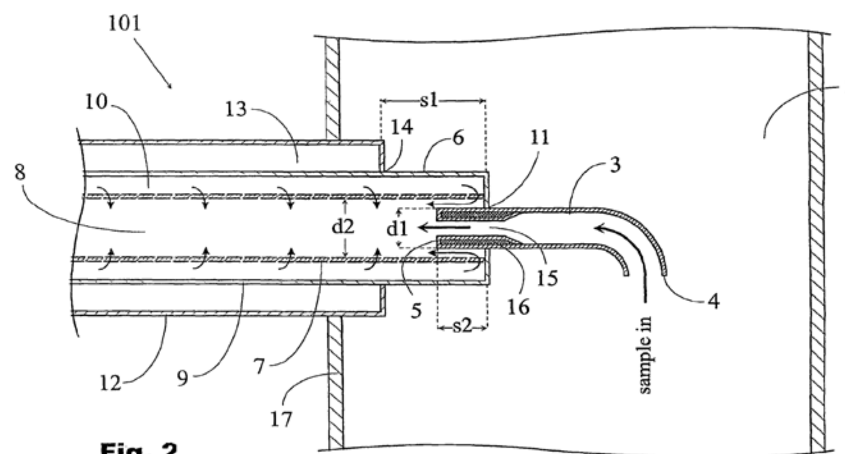


Fig. 2

Tar ?

Traditionally obtained by dry distillation of wood (slow pyrolysis)

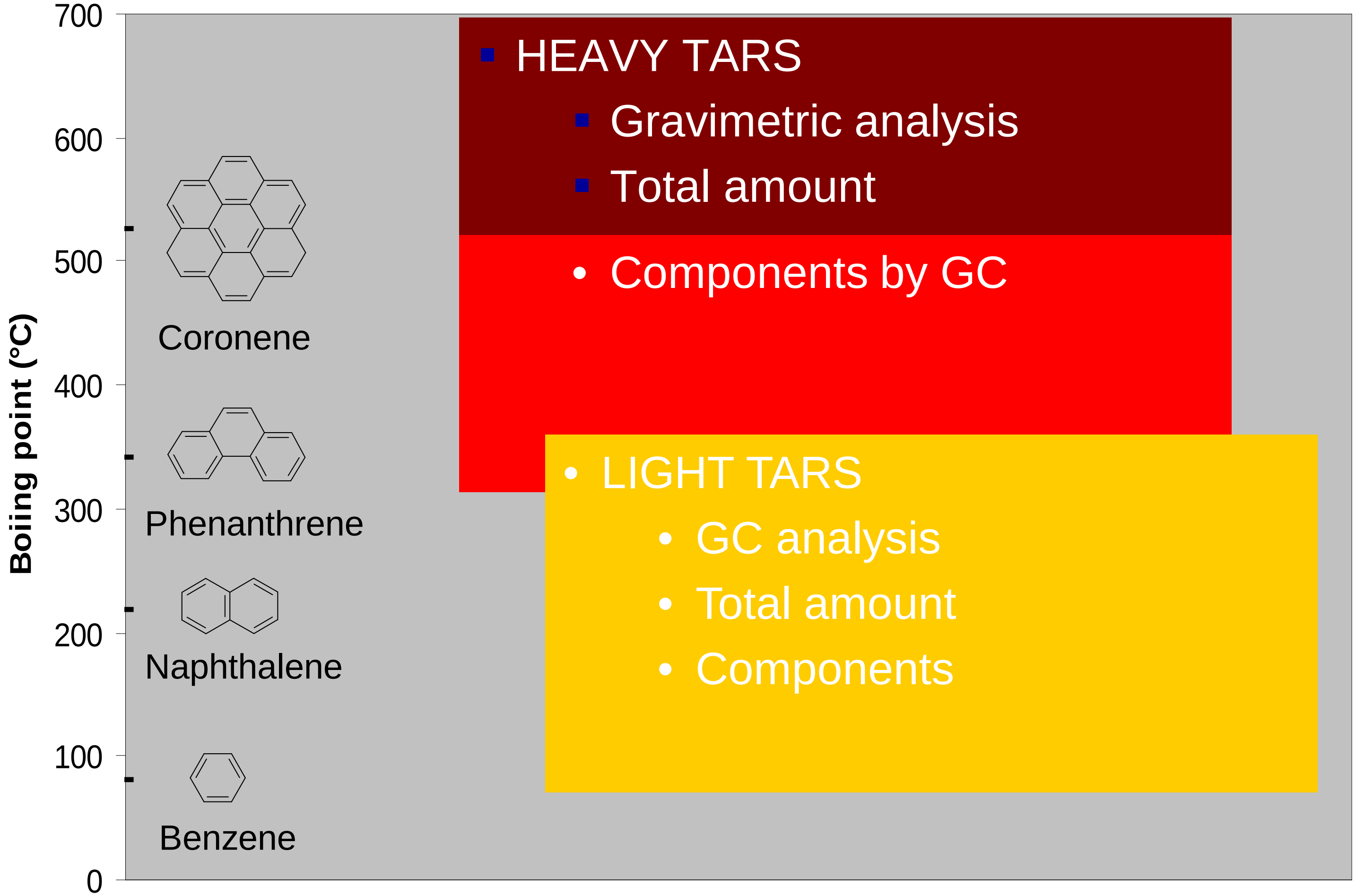
- Paint

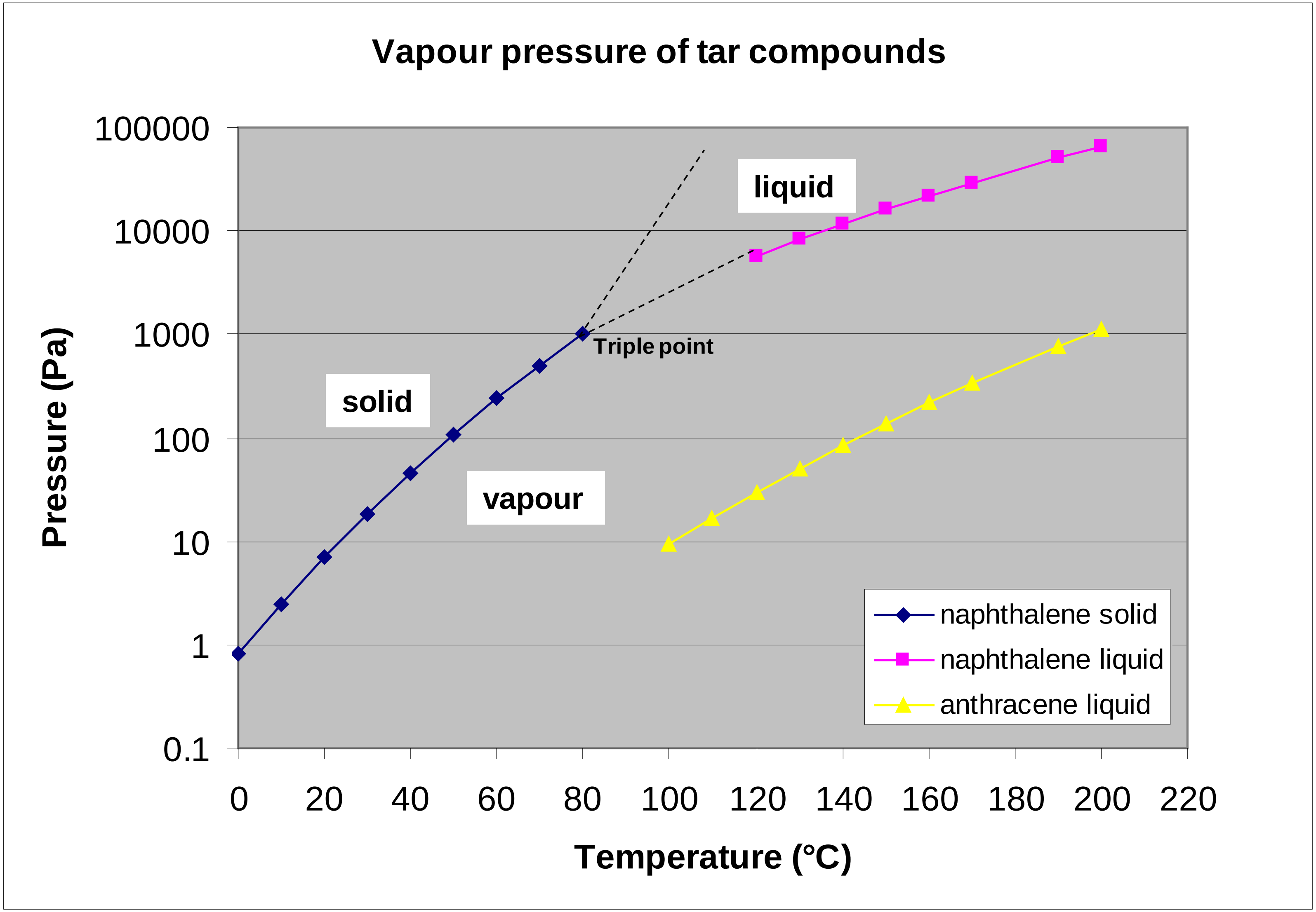
- Multipurpose substance:

”*if sauna, vodka and tar won't help, the disease is fatal*”

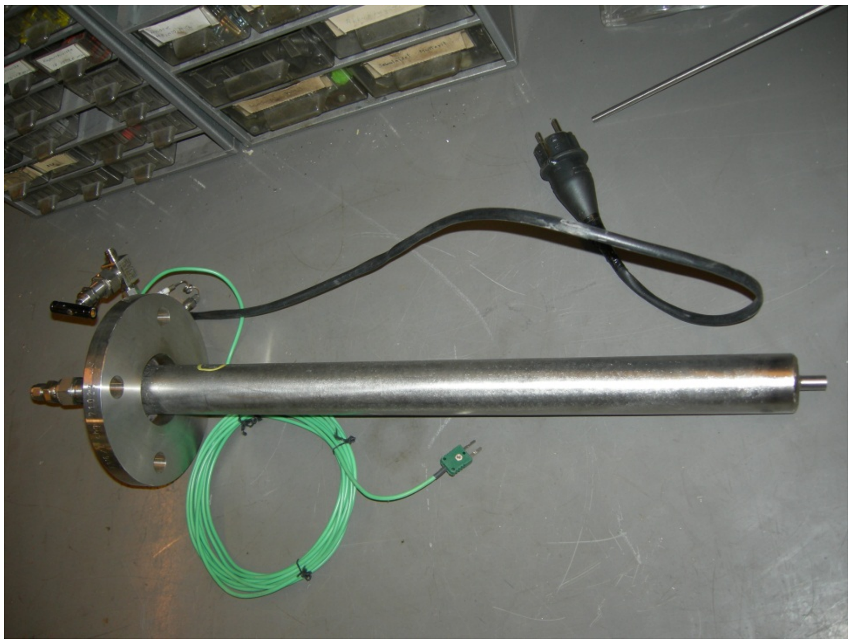
Pentti Vesterinen operating a tar-burning pit in the late 19th century

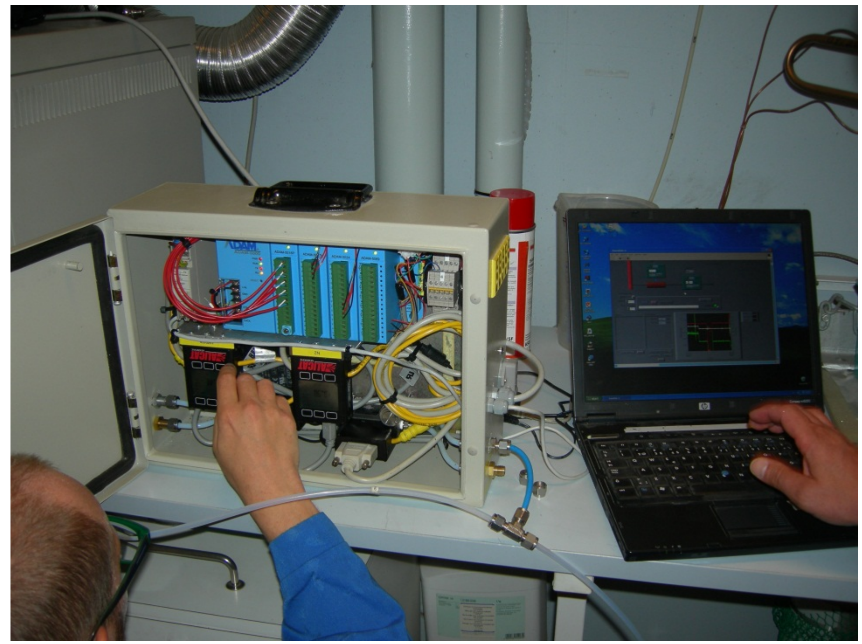
Tar characterization




Vapour pressure of tar compounds
Pressure (Pa)
100000
10000
1000
100
10
1
0.1
0
20
40
60
80
100
120
140
160
180
200
220
Temperature (°C)
liquid
solid
vapour
Triple point
naphthalene solid
naphthalene liquid
anthracene liquid

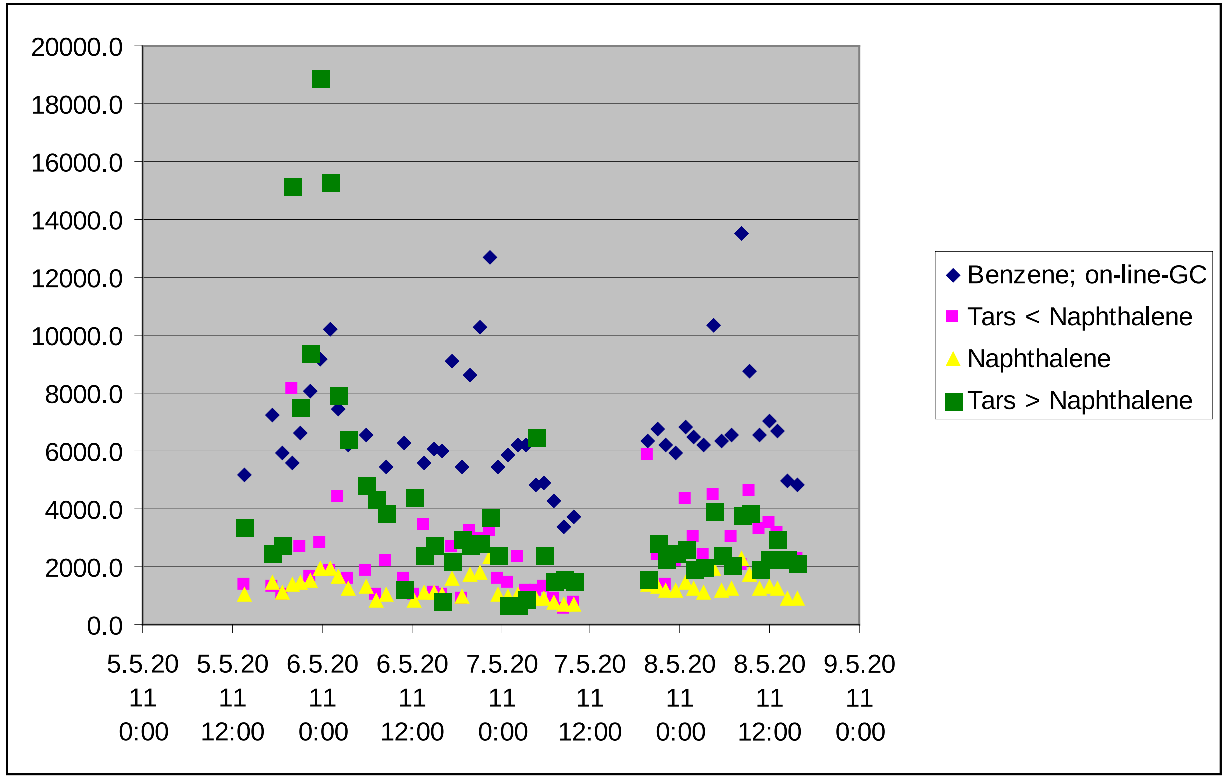
Dilution sampling probe with control unit





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

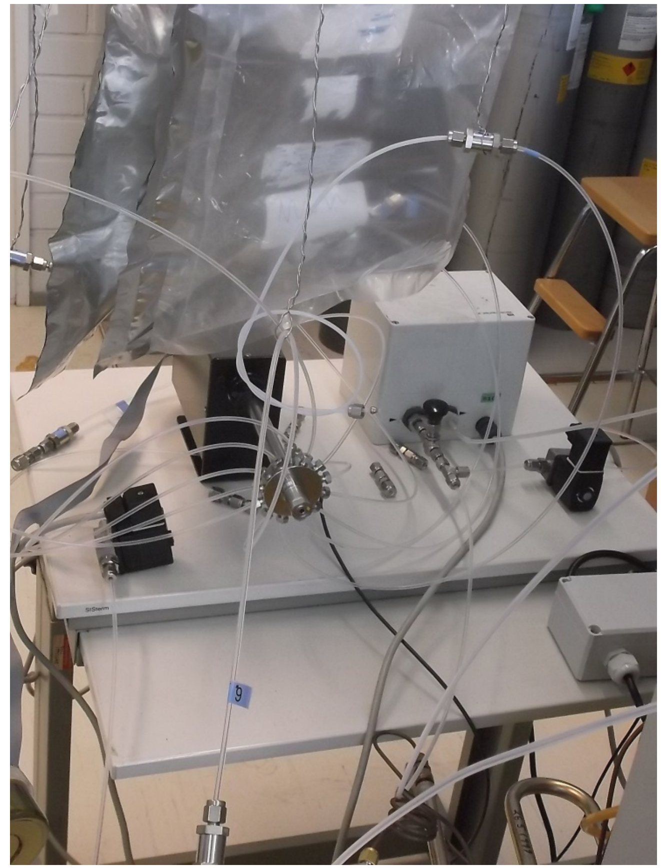
b) Commercial gasifier

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

Other tools for gasification gas analysis in use at VTT

Automatization of gas sampling bag analysis

- It is easy to automate gas sampling bag analysis using multiport valves and a USB-relay box
- At VTT results are collected next morning using Excel-macros
- The same system can be used for on-line analysis of several points of the process

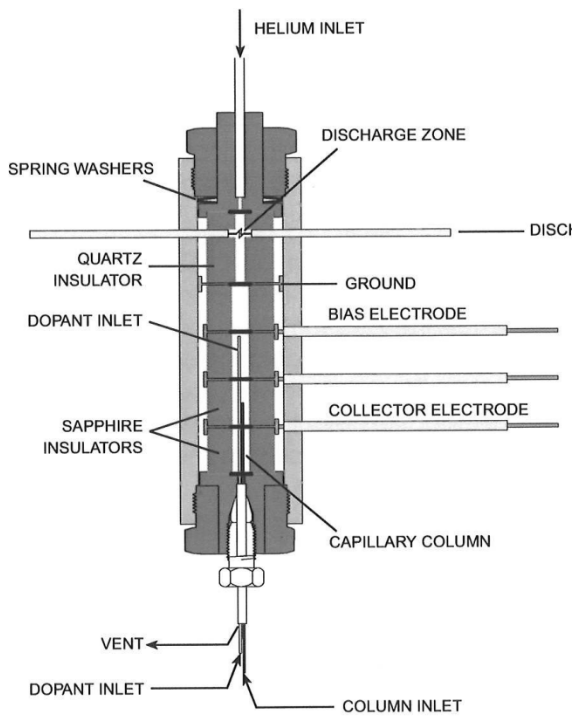


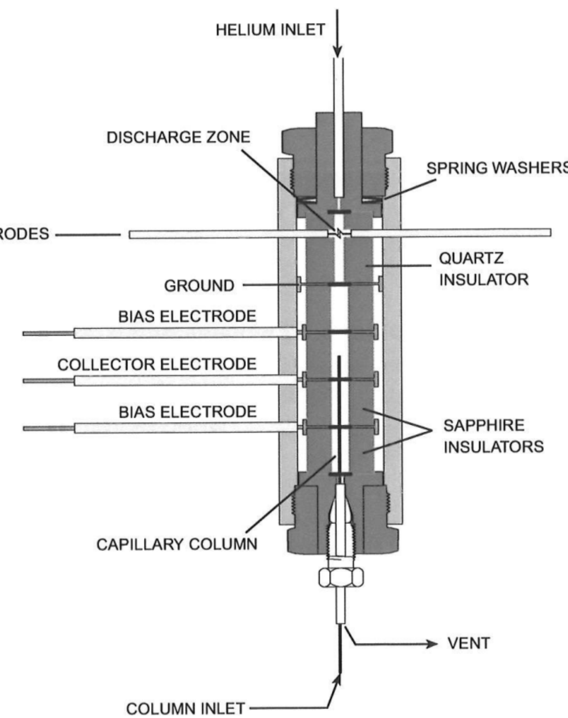
Pulsed Discharge Detector (PDD)

- Three detectors in one:
  - Helium Ionization (PDHID)
    - Highly sensitive universal detector
  - Photoionization (PDPID)
    - Three possible dopants (Ar, Kr, Xe)
    - Xe-PID detects compounds with IP<9.6 eV
  - Electron Capture Mode (ECD)
    - Good for halogen compounds
- At VTT first tests have been done on the analysis of:
  - CO, H_2O, CO_2, H_2S, NH_3, O_2, HCl
  - First results are promising

PDD

From Vici Valco

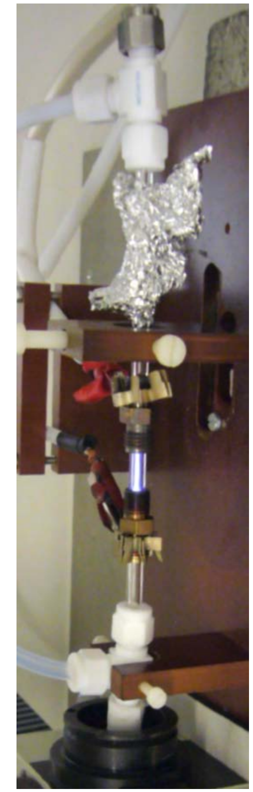




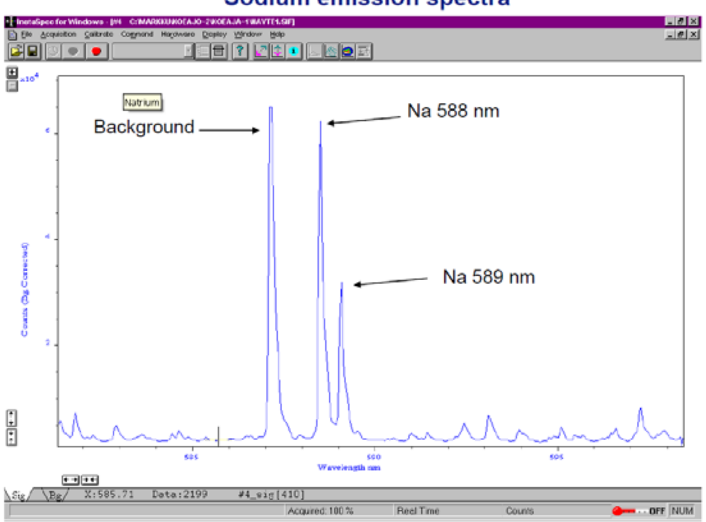
ECD-mode PDHID-mode

Development of a cheap and robust ICP-method for the on-line metal analysis

- ICP can be used for the simultaneous analysis of several metals (Na, Fe, Ni, Cu, Zn, Sb…)
- Plasma is generated by using power transistors by ramping the freguency until resonance is achieved (VTT's patent)
- Preferably a commercial ICP could be used
- Typical bands of various metals can be detected not only from a dry gas but also from wet gas or liquid solutions
- Method was successfully tested with real gasification gas

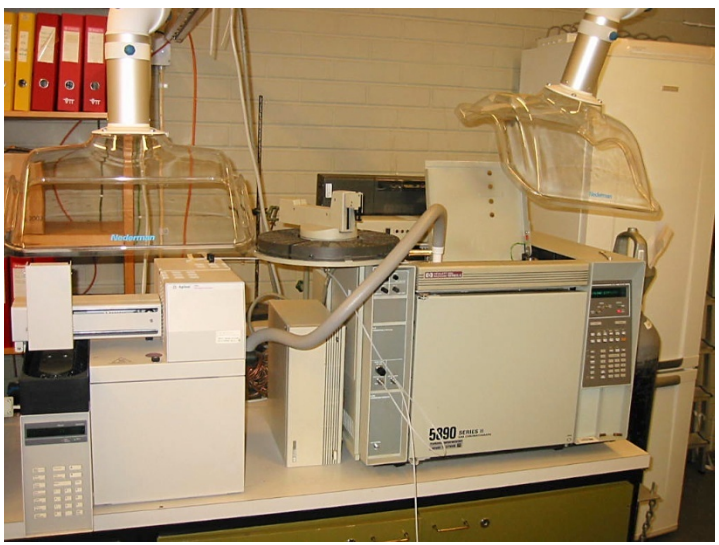


Sodium emission spectra

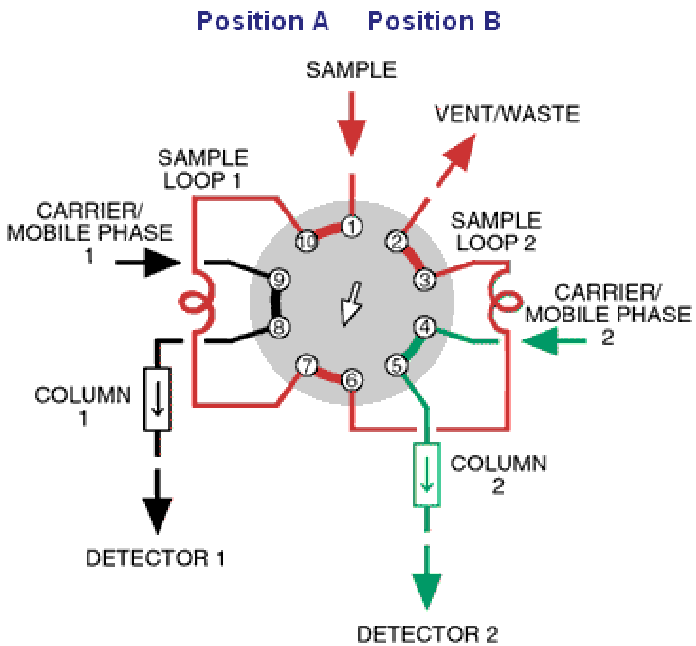


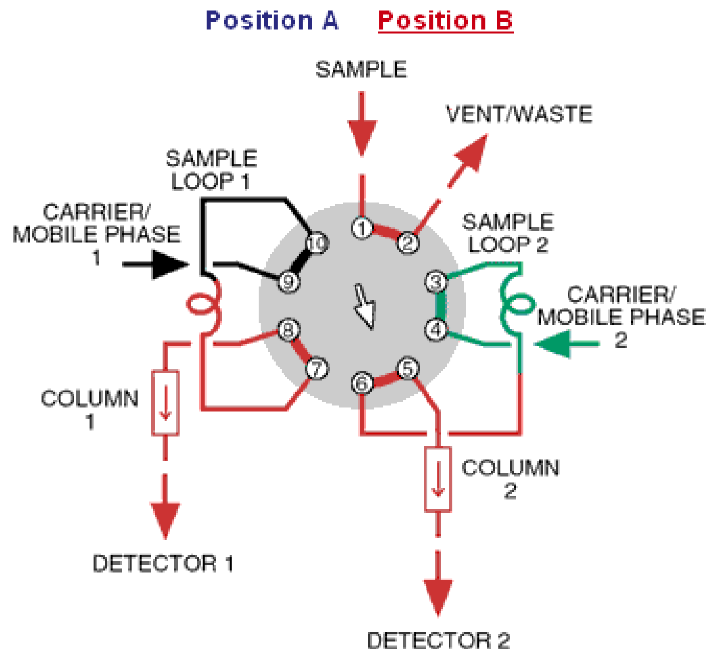
Analysis of HCN using static head space-technique (HS/GC-FID)

- 5 ml of 1:2 H_2SO_4 / water is injected to a gas tight 20 ml ampoule. The ampoule is sealed with a septum cap. 1 ml of sample (pH = 12) is injected through the septum on the H_2SO_4-solution.
- The sample ampoule is heated in the HS-apparatus at 80 °C for 5 min and then injected to GC-FID-analysis



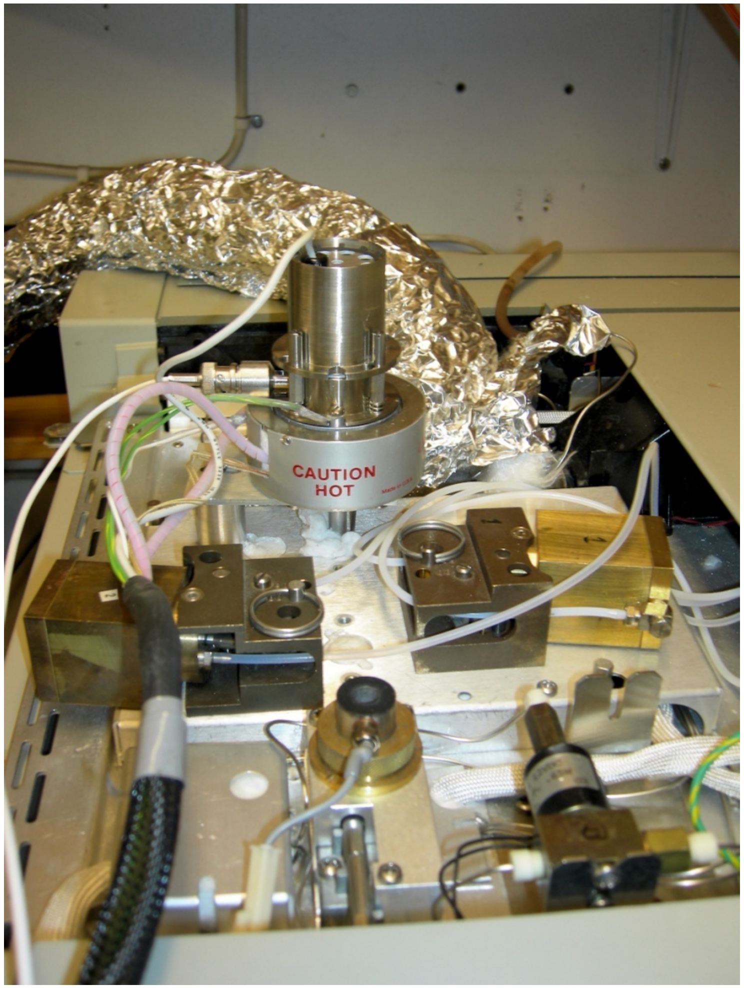
On-line analysis of tars, water and ammonia

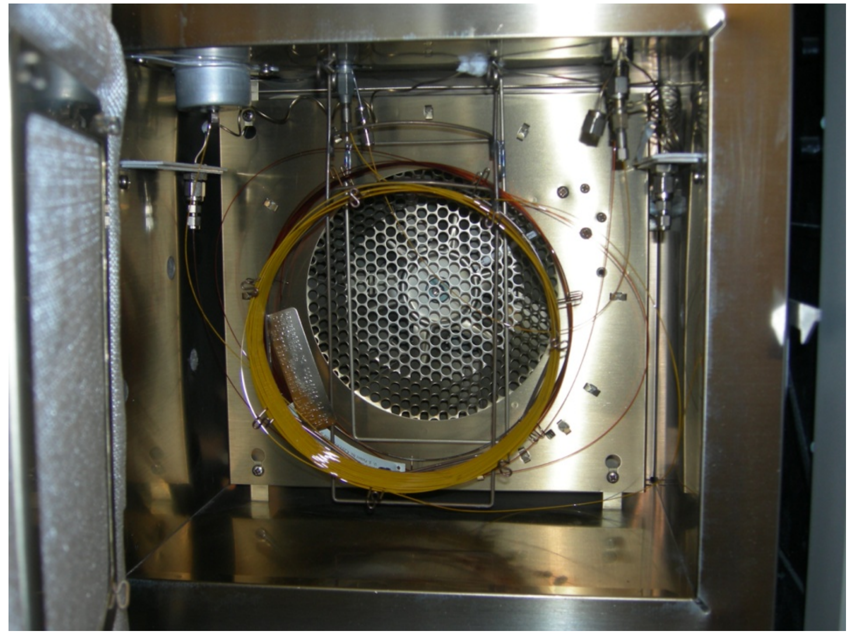




Simultaneous injection to two different columns:
Column 1: HP-1 for the analysis of hydrocarbons (FID)
Column 2: Poraplot-Q for the analysis of water (TCD) and ammonia (PID). TCD and PID in series.

On-line analysis of tars, water and ammonia






TECHNOLOGY FOR BUSINESS

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

VTT's new Gasification and Pyrolysis Platforms

- VTT will move it's Gasification and Pyrolysis test facilities to an industrial area in Kivenlahti, Espoo
- New pilot plants will also be constructed
- Start-up at new site in Q4/2014
- Efficient development from laboratory to industrial realization

Horizon 2020-projects (2015-2020)
- Biofuels for transport sector, renewable chemicals
- Fuel gas & pyrolysis oil for CHP and industrial applicatio
- Waste-to-Energy with material recovery

VTT RES-Infra Investment
New R&D Platform
2013-2015

Industrial projects
- Pyrolysis and gasification R&D
- Testing and piloting services
- Platform for new pilot plants

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

BIORUUKKI - New RESInfra Pilot Centre
Location: Kiviruukki industrial area, Kivenlahti/Espoo