Tar generation by ethene pyrolysis

Gas Analysis webinar, March 21st 2014

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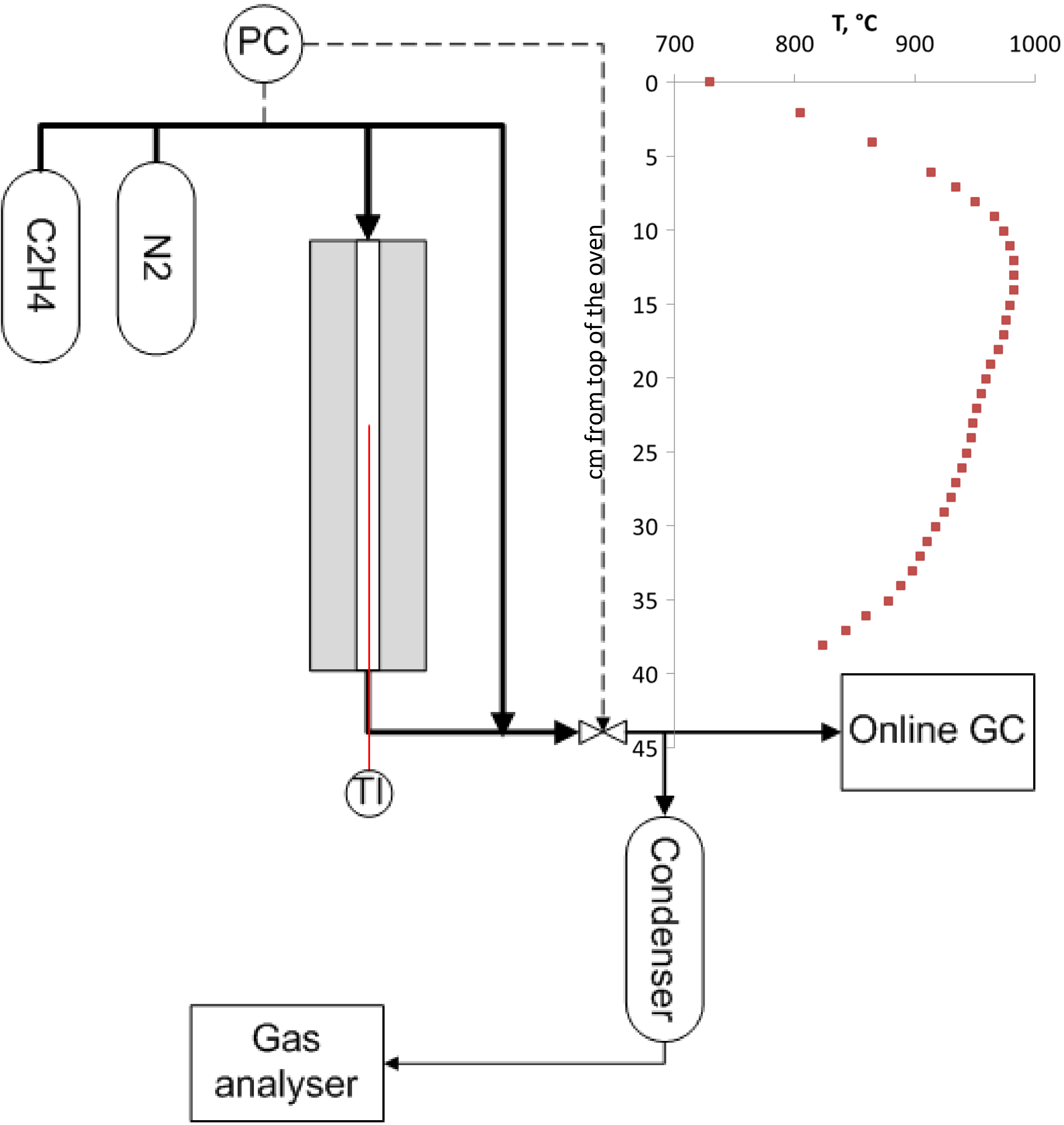
Background

- 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

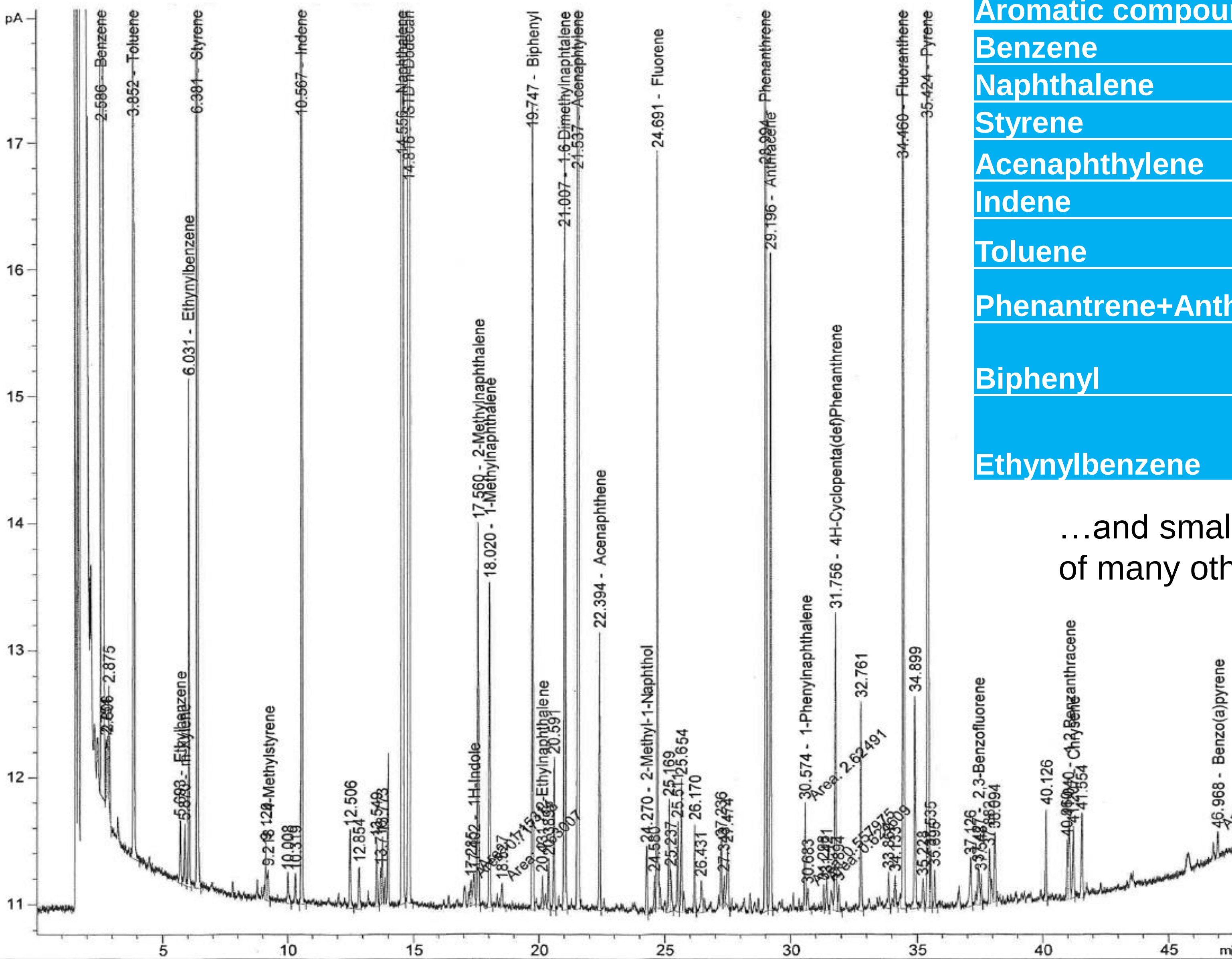
Laboratory set-up and conditions



- Feed: 5 vol-% ethene in N2
- 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

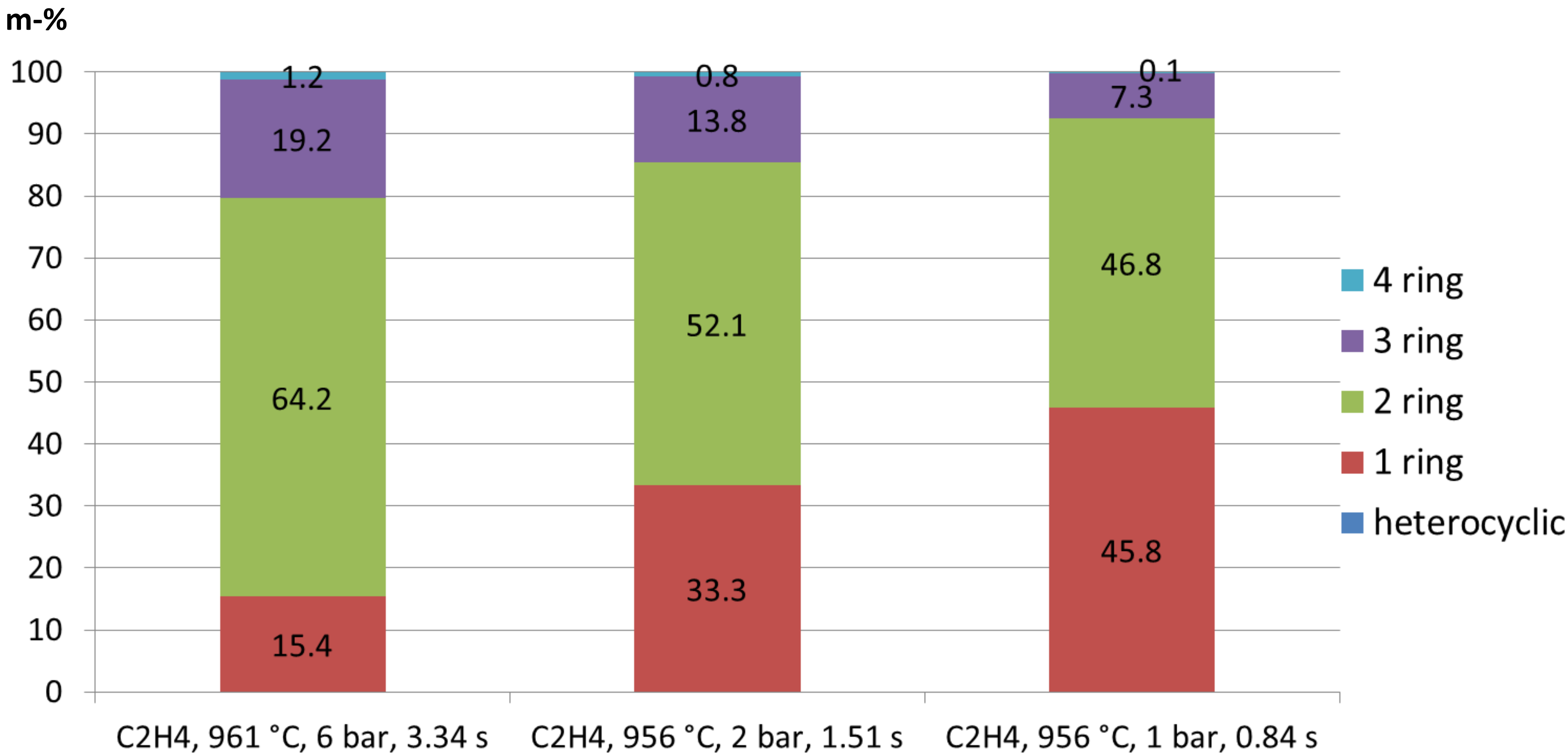
C_2H_4, 961 °C, 6 bar, 3.34 s



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)

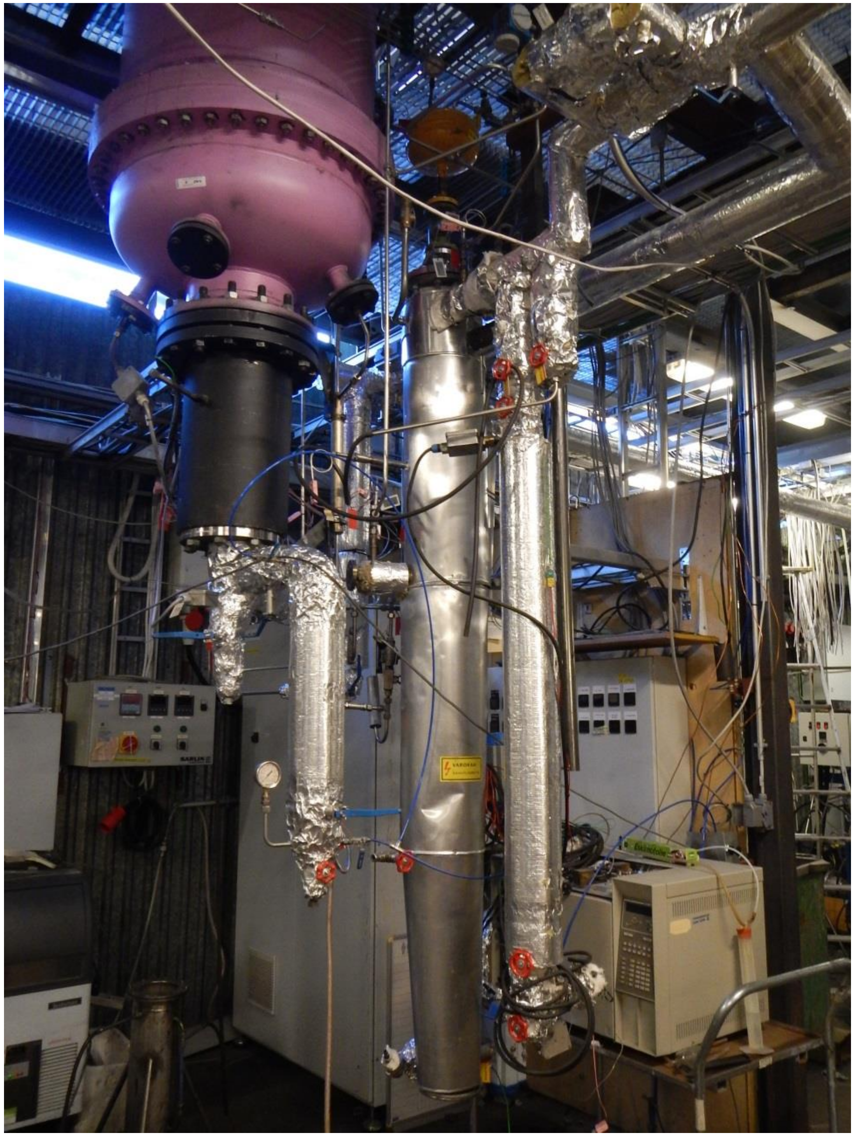
Generation of realistic tar-laden gasification gas in the ‘HOTPURI’-reactor

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
    4. Also on-line tar measurement was used

HOTPURI reactor

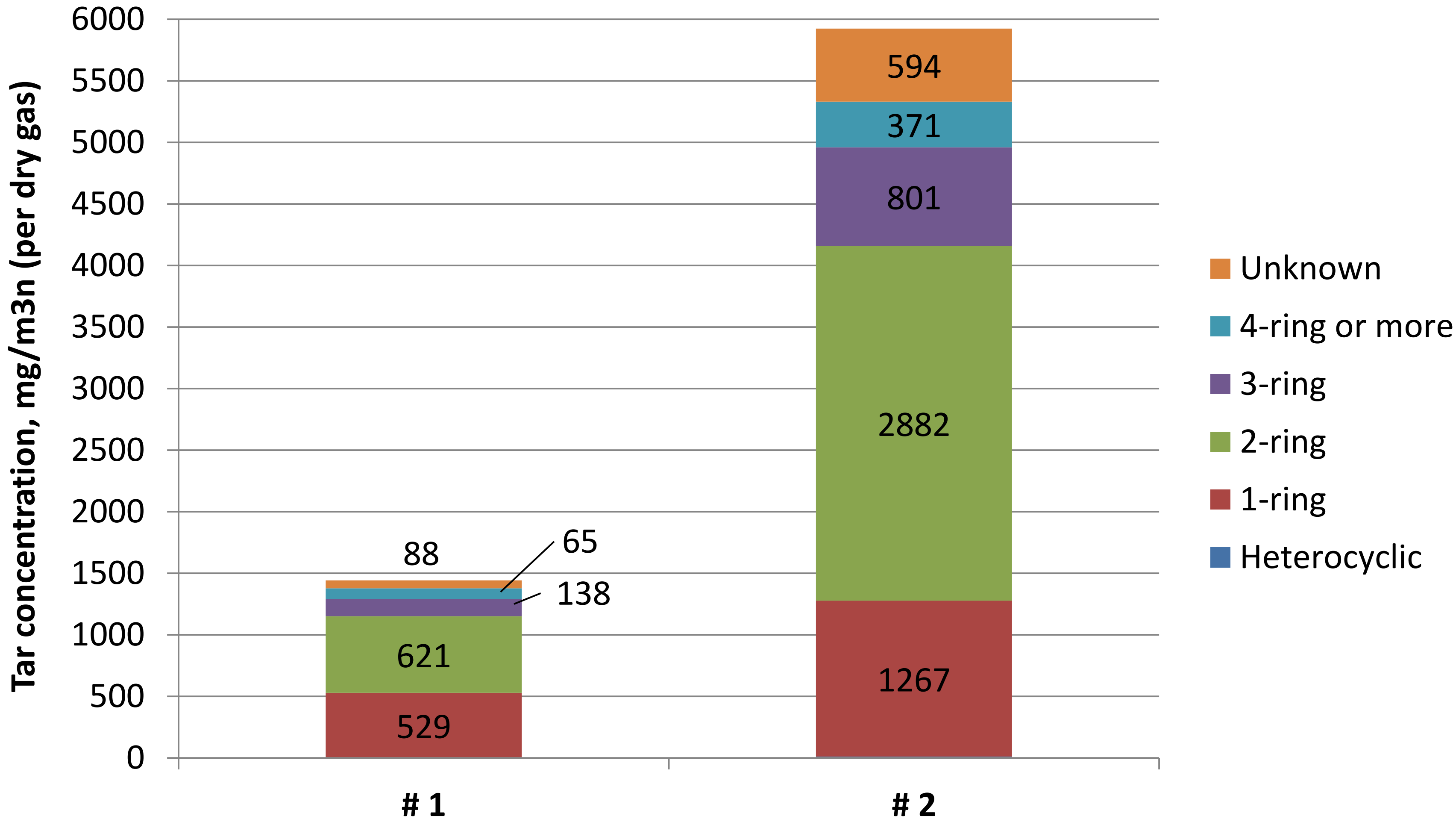


Examples of gas and tar composition

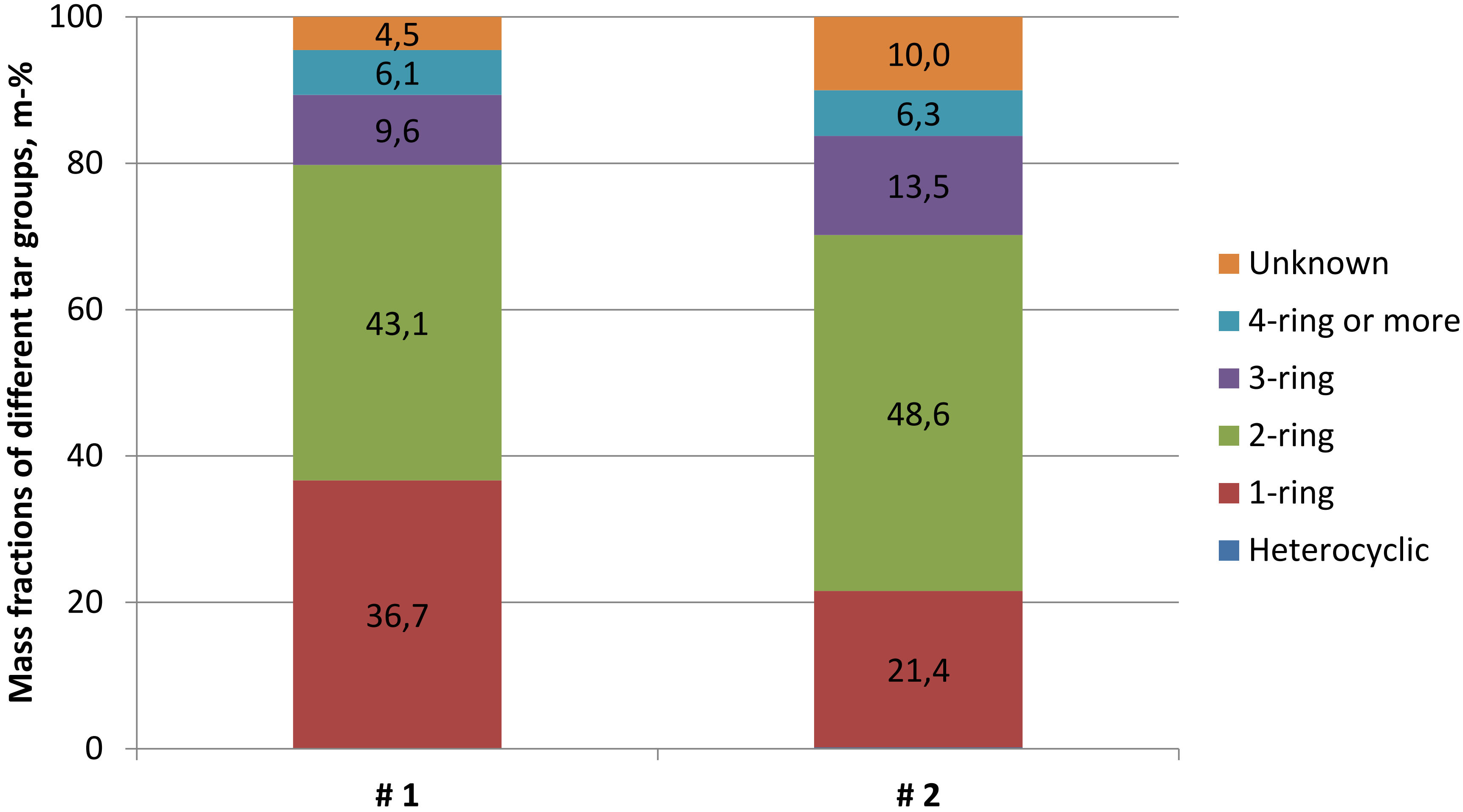
- The produced gas contained in excess of methane as the reactions conditions and feed gas ratios were not tuned for efficient conversion of natural gas. The tar yield was more important for our purposes.
- In addition to the main gas compounds, benzene and tars, also soot was formed.

TEST	# 1	# 2
Max temp in reactor, °C (appr.)	960	1100
Pressure	atmospheric	atmospheric
Residence time, s	> 3	> 4
FEED GAS COMP.	**m-%**	**m-%**
CH4	28,9	24,5
C2H4	10,4	21,1
O2	22,7	18,1
H2O	38,0	36,4
PRODUCT GAS COMP. (dry basis)	**vol-%**	**vol-%**
CO	13,9	18,9
CO2	12,7	8,6
H2	30,8	44,0
CH4	***36,7***	***24,6***
C2H2	0,1	0,1
C2H4	5,4	3,6
C2H6	0,29	0,19
C3-C5Hx	0,09	0,03
H2O, 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***

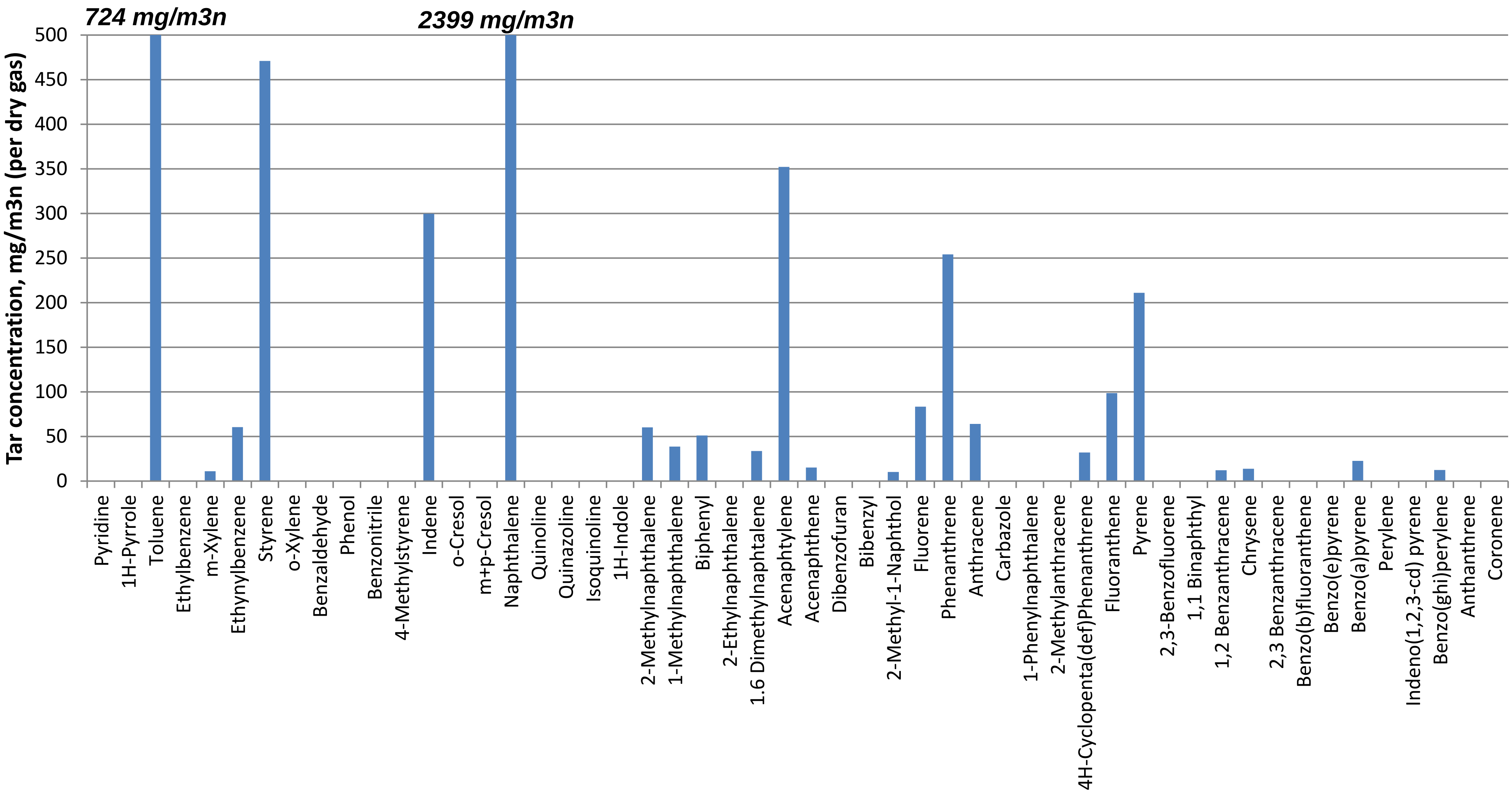
Examples of tar (excl. benzene) composition (1)



Examples of tar composition (2)

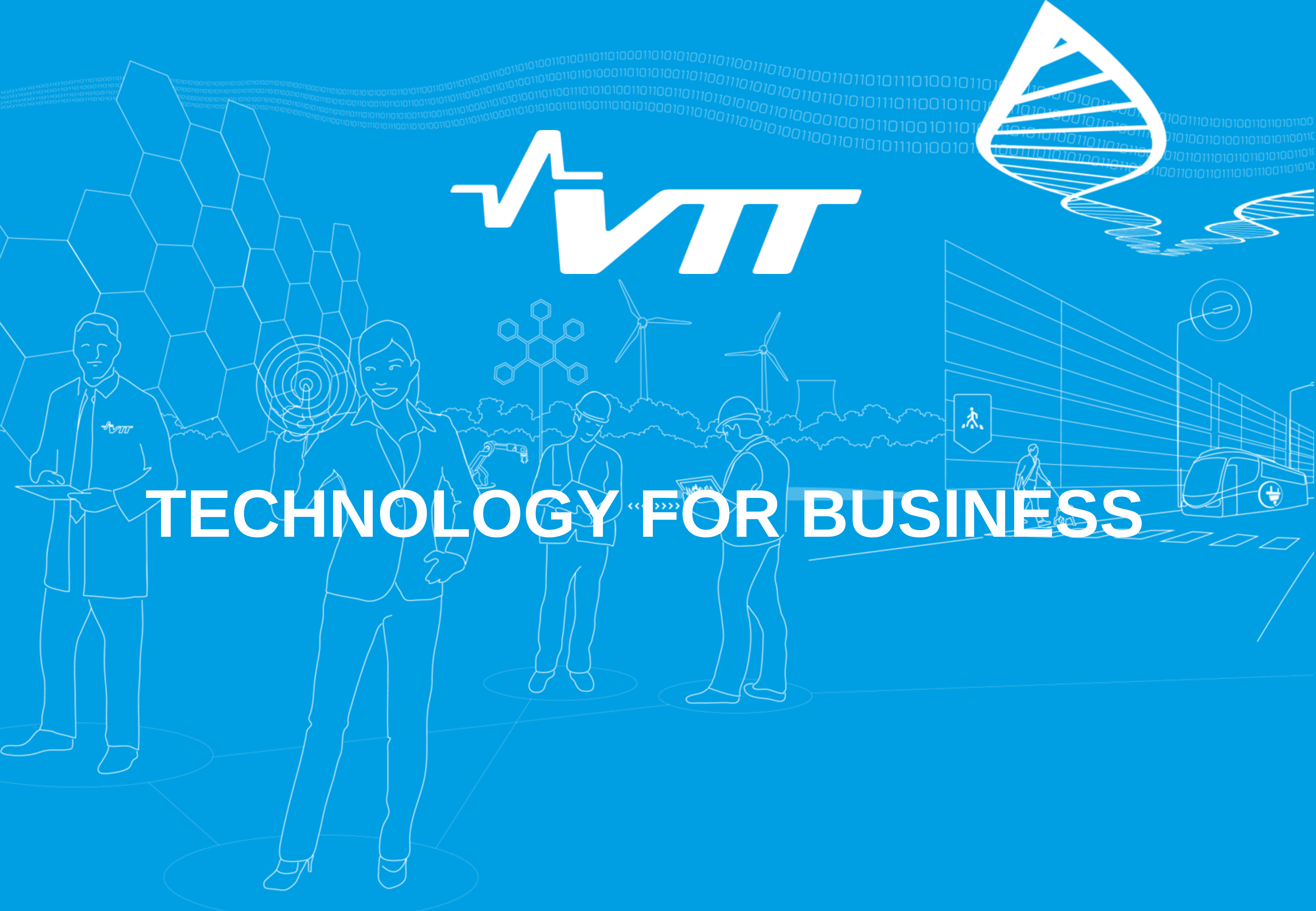


Examples of tar composition (3)
- Tar compounds in test # 2



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.
- No heterocyclic tar compounds were formed in lab-scale studies and their relative amount in HOTPURI tests was also low, max. 0.2 m-%.
- 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.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