HIGHBIO - INTERREG NORD
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Högförädlade bioenergiprodukter via förgasning
Korkeasti jalostettuja bioenergiatuotteita kaasutuksen kautta

EUROPEAN UNION
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Determination of tars in syngas

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Syngas

- The main product from gasification of biomass is syngas
- Clean syngas is a mixture of hydrogen (H2) and carbon monoxide (CO) and carbon dioxide (CO2)

- Tar is a contaminant that will affect future use of the gas,
  - high tar concentration can hinder the use of syngas in energy/power production and as a raw gas in chemical synthesis

The use of syngas from biomass gasification

- The analytical needs depends on the future use of the syngas:
  - If syngas is used for heat production, a measurement of heat values is often sufficient (for gas and for wood chips (fuel))
  - If the syngas is used for GTL conversion, at least the total concentration of tars in the gas should be known

Definition of tars

- **Definition:** tars are organic compounds with molecular masses higher than benzene ($M_{benzene}$= 76 g/mol)

- In fact tars are mixtures of organics and can contain hundreds of different compounds, mostly cyclic and polycyclic

PAH Structures

Pericondensed
(More than one internal Carbon node)

Pyrene
$C_{16}H_{10}$

Coronene
$C_{24}H_{12}$

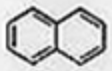
Perylene
$C_{20}H_{12}$

Benzo[ghi]perylene
$C_{22}H_{12}$

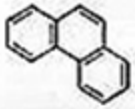
Antanthrene
$C_{22}H_{12}$

Ovalene
$C_{32}H_{14}$

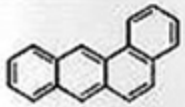
Catacondensed
(No internal Carbon vertices)



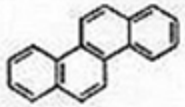
Naphthalene
$C_{10}H_8$



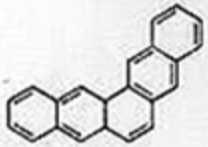
Phenanthrene
$C_{14}H_{10}$



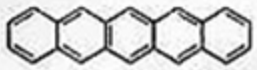
Tetraphene
$C_{18}H_{12}$



Chrysene
$C_{18}H_{12}$

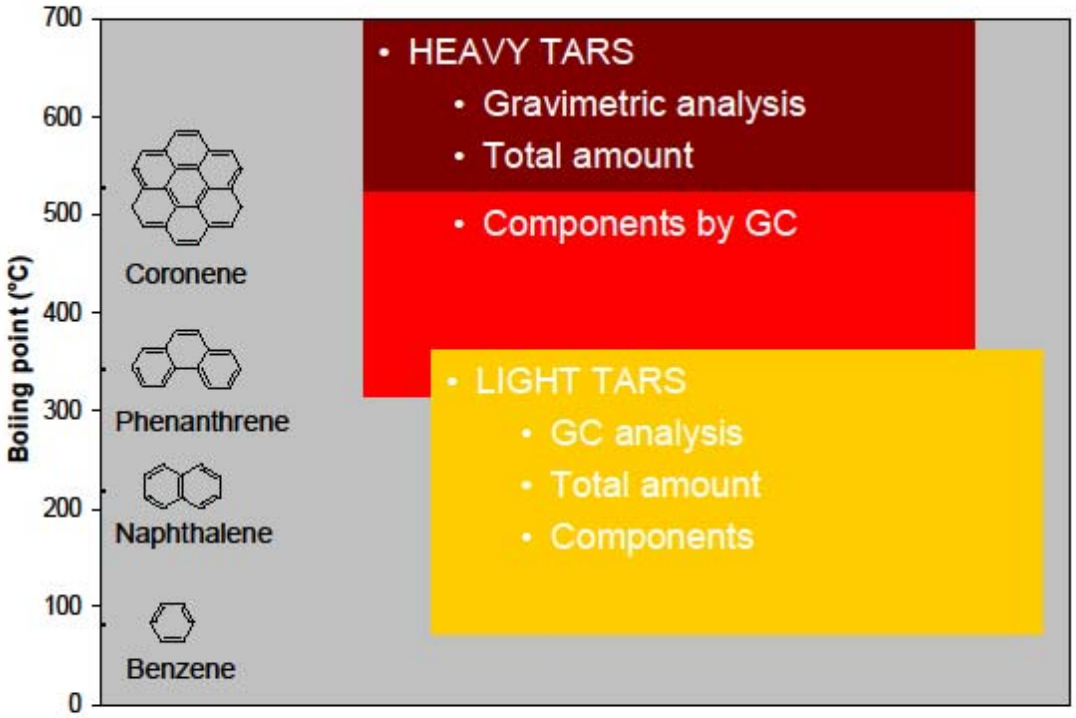


Pentaphene
$C_{22}H_{14}$



Pentacene
$C_{22}H_{14}$

Tar characterization



Tar content in syngas

- Tar content in syntheis gas can vary from below 1% to 20 % of wood mass dependig on
  - Source of biomass
  - Gasification process used
  - Gasification process parameters

Tar content as a function of gasification temperature

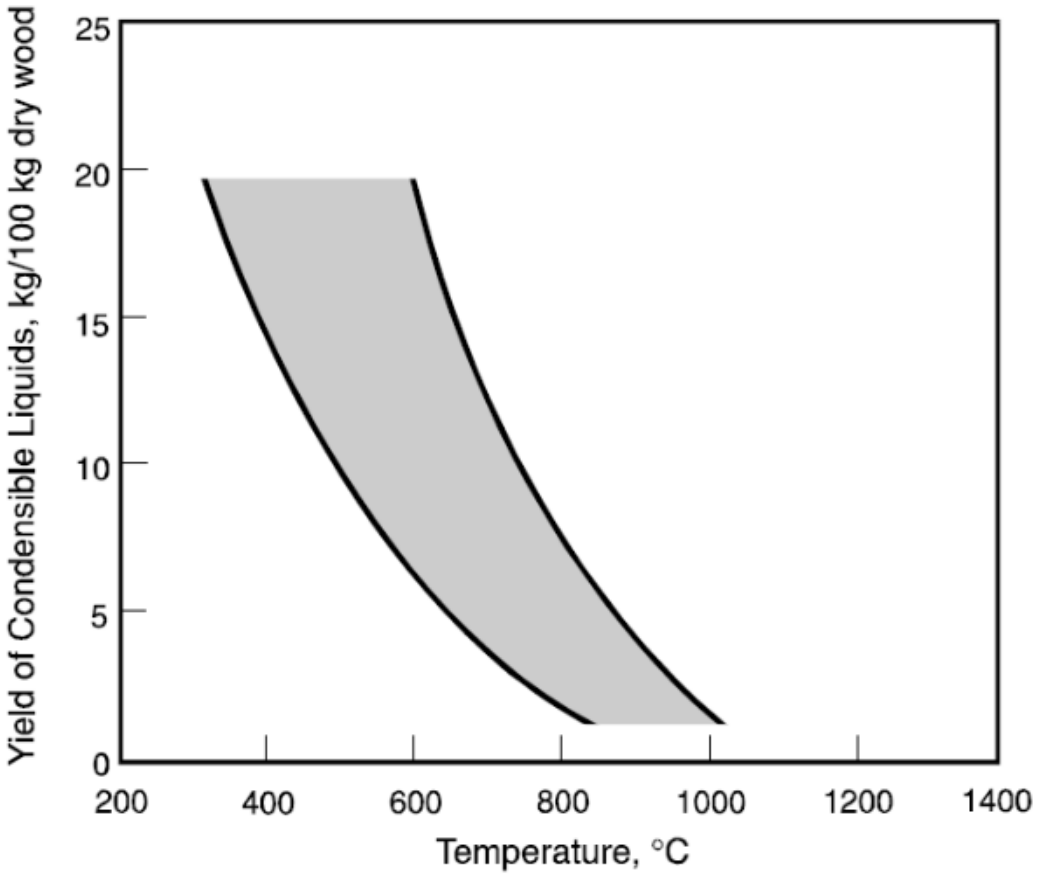


Figure 2.3. "Tar" yield as a function of the maximum temperature exposure (Baker et al. 1988).

”Maturation” of tars

- Not only the amount of tars will change during the gasification process

- But also the composition of tars will change

”Maturation” of tars

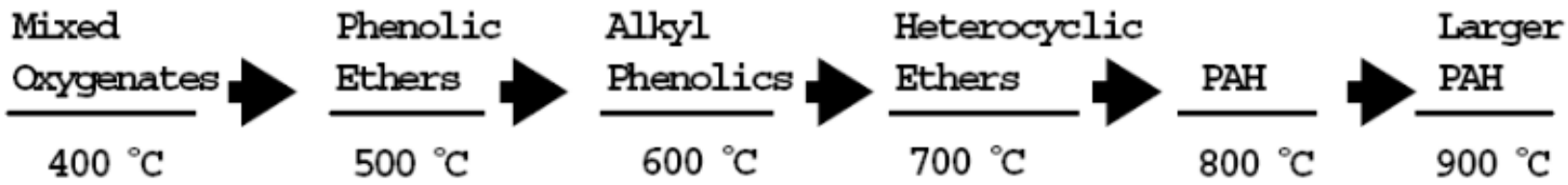


Figure 2.2. “Tar” maturation scheme proposed by Elliott (1988).

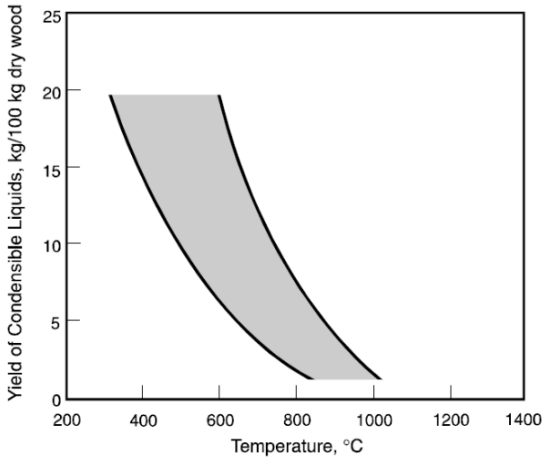


Figure 2.3. “Tar” yield as a function of the maximum temperature exposure (Baker et al. 1988).

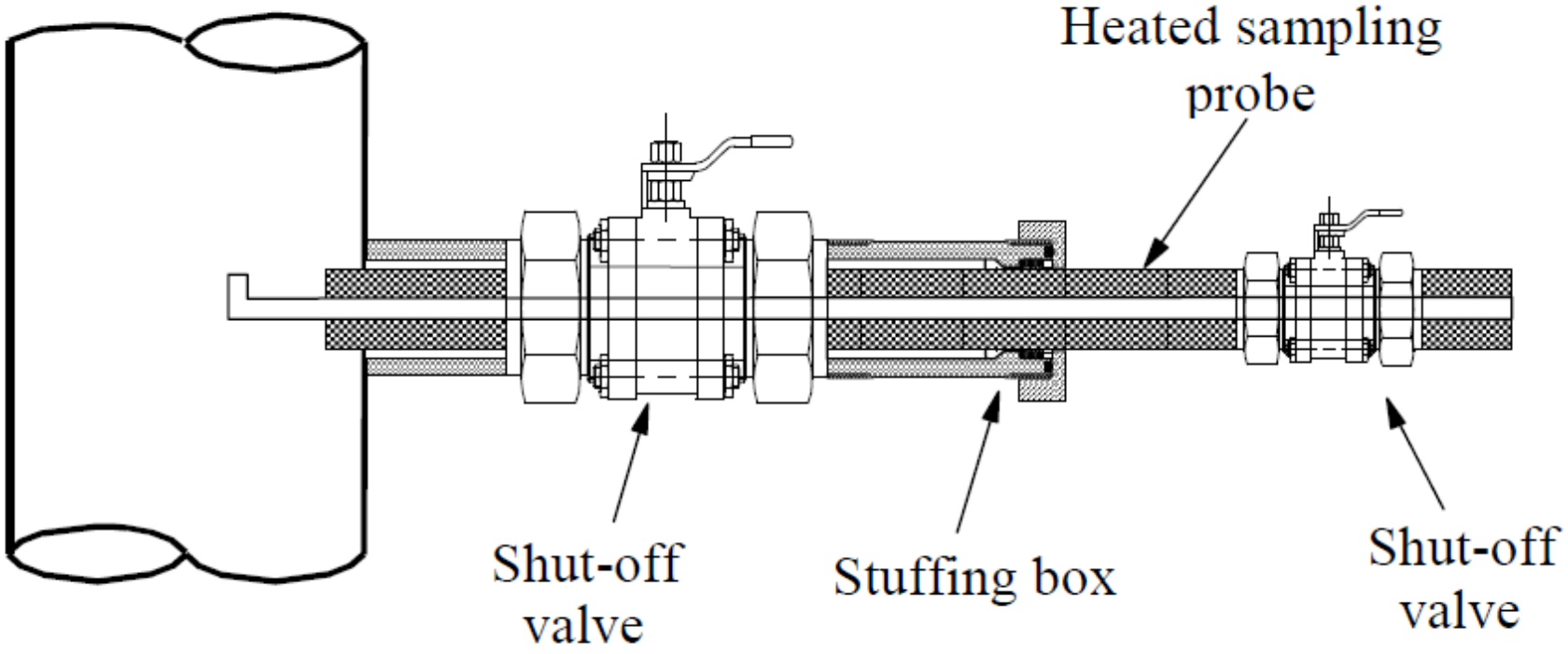
Analytical process

- Sampling
- Sample storage and treatment
- Method calibration (standardisation)
- Sample analysis
- Calculations and reporting

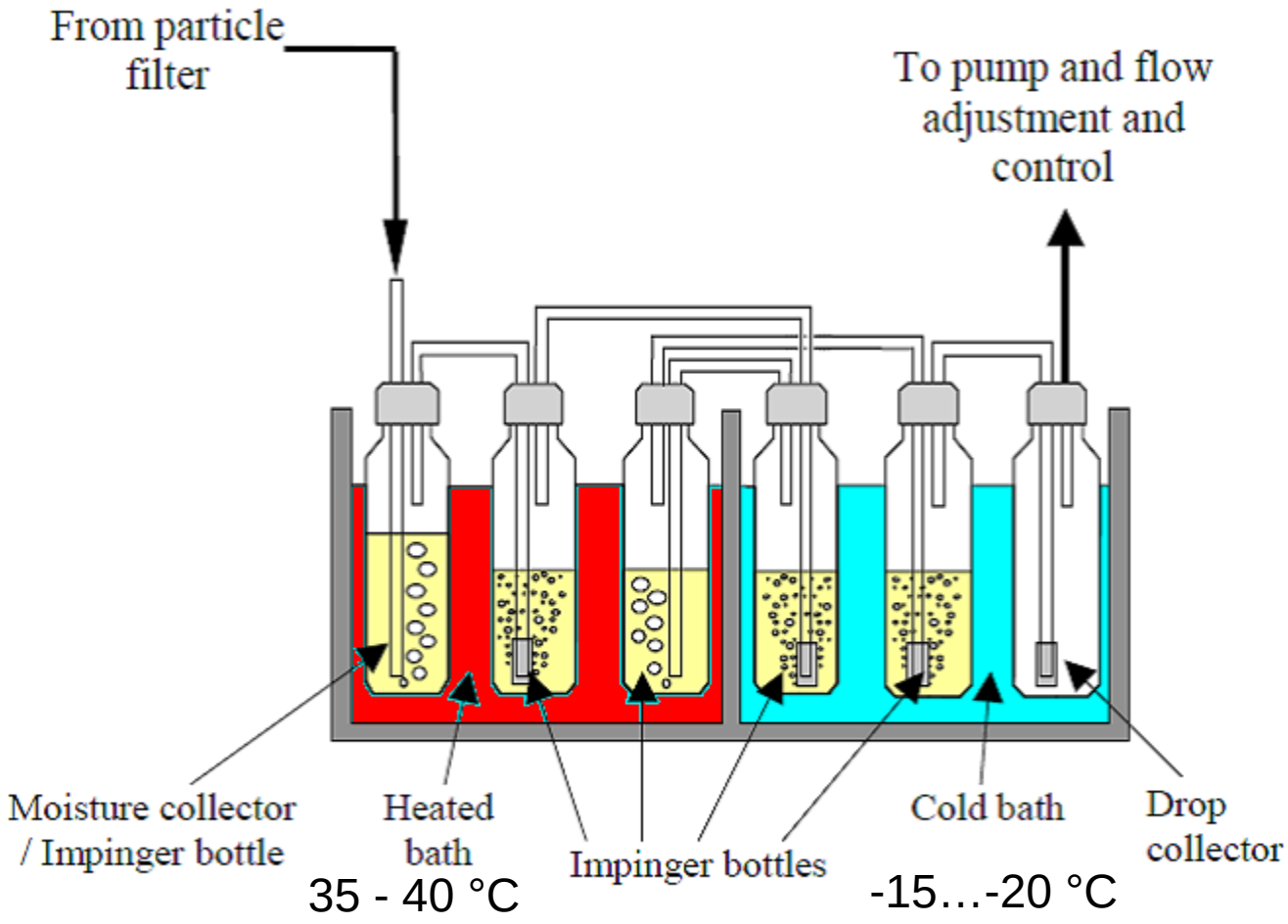
Tar sampling line

- consists of
  - sampling probe (heated),
  - filter for particulates
  - moisture collector, (heated)
  - absorption bottles
  - equipment to measure gasflow, sampling time, gas pressure and temperature

Tar sampling - Sampling probe



Absorbtion vessels



- After sampling, isopropanol (IPA) solutions from all bottles are combined, flasks are washed with IPA

- Combined content is stored at 5ºC protected from light

Analysis

- Analysis is performed with GC-MS or GC-FID
- Internal or external standard can be used for method calibration
- Use of internal standard (1,2-difenylbenzene) gives better precision
- Compounds are calculated as naphthalene equivalents
- In this method tars are compounds eluating between heptane (C7) and triacontan (C30)

GC-parameters

- **Column:** 30 m – 60 m, ID 0,25 – 0,32 mm, (5% diphenyl/95% dimethylsiloxan).
- **Oven:** 50 °C (5 min hold), 8 °C/min to 325 °C, 325 °C (5 min hold)
- **Injection:** 1 – 2 µl, temperature 275 °C, split 1:75
- **Detector:** FID at 300 °C
- **Carrier***:* Helium, 20 – 40 cm/s
- More parameters on INFO 29 and 30

Calculations

$$m_{TOT} = \left(\frac{m_{istd}}{K} \right) \cdot \left\{ \left(\frac{A_{TOT}}{A_{istd}} \right) - B \right\}$$

$$C_{TOT} = \frac{m_{TOT}}{V_{NTP}}$$

Summary of analysis methods

Analysis	*Online:*	*Offline:*
H_2, O_2, CO, CO_2, CH_4, N_2	a) continuous gas analyzers b) RGA-GC c) Micro-GC	Sampling bag → GC-TCD/FID
C_1–C_6 HC's, benzene, toluene	GC-FID	Sampling bag → GC-FID
Benzene, toluene, naphthalene	MS	
In laboratory: H_2O, CO, CO_2, CH_4, C_1–C_6 HC's, Benzene, Toluene	FT-IR, GC-FID	
Light tars	Rapid method with a GC-FID	IPA-solution → GC (rapid or multicomponent analysis)
H_2O		GC-TCD (from light tar sample) Gravimetric analysis from condensate
Heavy tars		Gravimetric methods
NH_3	GC-TCD	Kjeldahl distillation from H_2SO_4-solution
CN^-		NaOH solution, distillation, ion-selective electrode
H_2S, COS	MS (H_2S)	Sampling bag → GC-FPD
HCl		IPA-solution → Capillary electroforesis
As, Sb, Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn, Tl, Sn, V (not Hg)		HNO_3 + IPA-solutions → ICP-AES, ICP-MS, GFAAS
Hg		4 % $K_2Cr_2O_7$ in 20 % HNO_3 → CVAAS
Alkalis		ICP from toluene and water
Particulates		Various methods

22

Litterature

- **Pieniniemi K (2008)** A short survey of tar sampling and analysis methods
- **HighBio** INFO 29 and 30

  https://ciweb.chydenius.fi/project_files/HighBio%20projekti%20INFO/INFO%20HighBio%20F29.pdf (SE)
  https://ciweb.chydenius.fi/project_files/HighBio%20INFO%20fr%C3%A5n%20projektet/INFO%20HighBio%2029.pdf (FI)
  https://ciweb.chydenius.fi/project_files/HighBio%20projekti%20INFO/INFO%20HighBio%20F30.pdf (SE)
  https://ciweb.chydenius.fi/project_files/HighBio%20INFO%20fr%C3%A5n%20projektet/INFO%20HighBio%2030.pdf (30)
- **Matti Reinikainen, Pekka Simell**: Synthesis Gas Characterization at VTT laboratories and test facilities
- **Milne and Evans (1998)** Biomass gasifier ”Tars”: Their nature, formation and conversion
- **Tiitto J (2008)**

Thank You!!!