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Tar measurement by the Solid Phase Adsorption (SPA) method

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Introduction

- Measurement of biomass tars after gasifier/gas clean-up, easy to use, low cost up to analysis
- Guideline method too cumbersome, only used by gasification <700°C
- Since 1998 ECN used & improved the SPA method (originally developed by KTH, Sweden)
- SPA measures Polycyclic Aromatic Hydrocarbons (PAHs) with MW 104 (styrene) to 300 (coronene)
- Reproducibility within 10% for most tar components

Sampling

- 100 ml gas at constant flow rate by automated syringe pump
- Sample syringe attached to pump by short tube
- Type of SPA: LC-NH2 (aminopropyl), 100mg
- Flow rate: 50 ml/min

Sample treatment

- Volatile compounds (BTEX) are not 100% adsorbed (pass through adsorbent, we use micro-GC for Benzene & Toluene)
- All other measured compounds (oxygenated compounds , N PAHs & PAHs without hetero atoms) adsorb & desorb well
- Heavy compounds (MW>300) do not evaporate sufficiently in a GC-FID and are not measured
- Analyse within few hours: <15% loss, BTEX more loss from column
- Storage @ -20°C to prevent evaporation from SPA, BTEX is lost, indene & phenol is slightly lost after 2 months
- Both column & needle are flushed with 2 x 1ml DCM

GC analysis

- Hot split injection on non polar GC column
- Detection with FID (Flame Ionization Detector)
- Calibration via internal standard (n-dodecane)
- Detection limit is 2.5 mg/m3 for 100 ml gas sample
- 33 compounds identified, other peaks labelled as ‘Unknowns’ & classified in 5 groups according to elution on the GC column

GC analysis

- Identified compounds

- Benzene
- 2-methyl-naphthalene
- Benzo(a)-anthracene
- Toluene
- 1-methyl-naphthalene
- Chrysene
- Ethylbenzene
- Biphenyl
- Benzo(b)-fluoranthene
- m/p-Xylene
- Ethenyl-naphthalene
- Benzo(k)-fluoranthene
- o-Xylene+Styrene
- Acenaphtylene
- Benzo(e)-pyrene
- Phenol
- Acenaphtene
- Benzo(a)-pyrene
- Indene+o-cresol
- Fluorene
- Perylene
- m/p-Cresol
- Phenanthrene
- Indeno(123-cd)-perylene
- Naphthalene
- Anthracene
- Dibenz(ah)-anthracene
- Quinoline
- Fluoranthene
- Benzo(ghi)-perylene
- Isoquinoline
- Pyrene
- Coronene

GC analysis

- Groups ‘Unknowns’ (based on location on GC chromatogram):
  - 1 Benzene to naphtalene
  - 2 Napthalene to phenantrene
  - 3 Phenanthrene to pyrene
  - 4 Pyrene to benzo(e)pyrene
  - 5 Benzo(e)pyrene to end

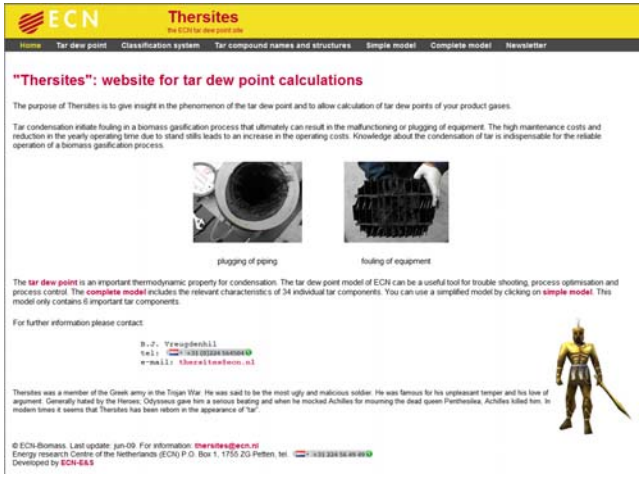
GC analysis

- Tar clasification system by ECN

Class 1	GC undetectable tars. This class includes the heaviest tars that condense at high temperature even at very low concentrations.
Class 2	Heterocyclic components (like phenol, pyridine, cresol). These are components that generally exhibit high water solubility, due to their polarity.
Class 3	Aromatic components. Light hydrocarbons that are not important in condensation and water solubility issues.
Class 4	Light polyaromatic hydrocarbons (2-3 rings PAH's). These components condense at relatively high concentrations and intermediate temperatures.
Class 5	Heavy polyaromatic hydrocarbons (4-5 rings PAH's). These components condense at relatively high temperature at low concentrations.

Calculation of the tar dew point

- Concentration of tar in a gas is assumed to be in thermodynamic equilibrium.
- For most of the 33 SPA tar components the vapour pressure data are known.
- The Antoine equation is used to determine for a mixture what the temperature is to keep all tar molecules in the gas phase.
- www.thersites.nl



Tar dew point model considerations

Advantages

- Model is a quick and simple to use
- Provides insight in the behavior of gas cleaning
- Takes mixtures into account.
- Verified with actual measured tar dew points

Disadvantages

- Limited to the range of input data (<200 °C)
- Only uses components with known Antoine constants
- Large amount of unknowns decreases the accuracy of the model

Considerations

- SPA warms up during sampling period: BTEX, Indeen and 1-ring sulphur compounds not quantitatively adsorbed.
- Sulphur compounds are measured by GC-FID on the lab
- Other adsorbents: maybe a C18, fenyl phase or carbon like materials adsorbs BTEX and PAHs better but eluting may be more difficult
- Blanc interference can be improved
- In combination met de micro-GC & GC-FID on the lab, we are satisfied with the current SPA method