



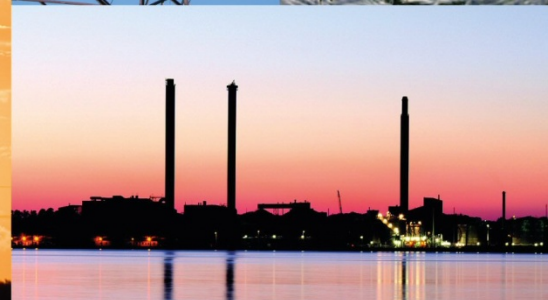
Energy research Centre of the Netherlands

Tar measurement by the Solid Phase Adsorption (SPA) method

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Tar measurement by the Solid Phase Adsorption (SPA) method



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 naphthalene
 - 2 Naphthalene to phenanthrene
 - 3 Phenanthrene to pyrene
 - 4 Pyrene to benzo(e)pyrene
 - 5 Benzo(e)pyrene to end

GC analysis

- Tar classification 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

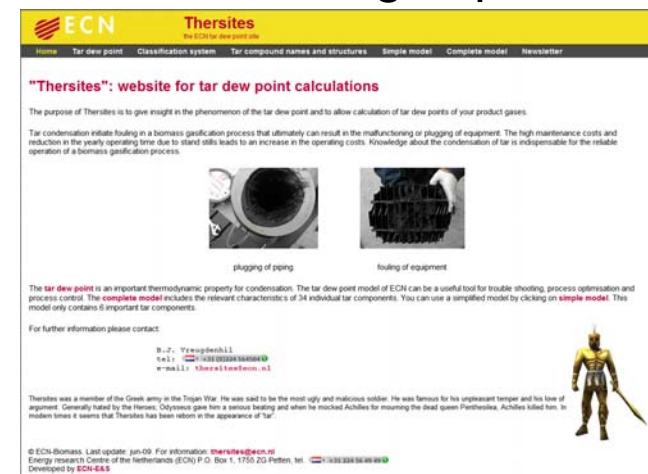
Light polyaromatic hydrocarbons (2-3 rings PAH's). These components condense at relatively high concentrations and intermediate temperatures.

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



The screenshot shows the homepage of the Thersites website. At the top, there is a yellow header with the ECN logo and the text "Thersites the ECH for the world wide". Below the header is a navigation menu with links: Home, Tar dew point, Classification system, Tar compound names and structures, Simple model, Complete model, and Newsletter. The main content area features the title "Thersites": website for tar dew point calculations. A paragraph explains the purpose of the website: to give insight in the phenomenon of the tar dew point and to allow calculation of tar dew points of your product gases. It also states that tar condensation initiates fouling in a biomass gasification process, which can lead to equipment malfunctioning or plugging, increasing maintenance costs and operating expenses. Two images illustrate "plugging of piping" and "fouling of equipment". Below these images, a paragraph describes the tar dew point model as an important thermodynamic property for condensation, used for troubleshooting, process optimization, and process control. It mentions that the complete model includes 34 individual tar components, while a simplified model is also available. Contact information is provided: P.O. 29000, Vrije Universiteit Amsterdam, and email: thersites@ecn.nl. A small image of a Greek warrior (Thersites) is shown on the right. At the bottom, there is a copyright notice: © ECH Biomass, Last update: jun-09, For information: thersites@ecn.nl, Energy research Centre of the Netherlands (ECN) P.O. Box 1, 1700 ZB Delft, the Netherlands, and Developed by ECH-E&S.

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