Tar measurements – developments towards further standardization

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Biofuels Research Infrastructure for Sharing Knowledge
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WP 7 Advanced measurement methods & operational procedures in thermo-chemical biomass conversion

Task 7.2 Tar sampling & analysis (KTH, ECN, JRC-IE, TUD)

Towards standardized analysis technique(s):

optimal sampling conditions for particle removal, flow, temperature under challenging biomass gasification conditions, moreover analysis

- KTH: on-line PID, heavy tar sampling & analysis, comparison with SPA sampling & GC analysis
- ECN: tar standard & SPA adaptations, (on-line dew point analyser)
- JRC-IE, GC-size exclusion, UV Fluorescence (heavy tar)
- TUD: online GC-FID/FID, BTX optimized SPA

pave the way for development of less elaborate, on-line?? practices via new protocols and following benchmarking! WP5 Protocols, Databases and Benchmarking
In the end of the nineties (last century) long discussions in scientific community (a.o. IEA, EU-FP5) ‘ending’ in:

Generic (unspecific) term for entity of all organic compounds present in the gasification product gas excluding gaseous hydrocarbons (C1 through C6)
What are the issues with tars?

Relatively low temperature gasifiers (FixB, [C]FB) cause tar issues (next to gasification product gas losses):

Pipe blocking

Process Equipment Fouling

Need to measure tars

Courtesy: www.thersites.nl (ECN)
## Tars classification

<table>
<thead>
<tr>
<th>Class</th>
<th>Type</th>
<th>Examples</th>
<th>Most relevant in dew point</th>
<th>Most relevant in water pollution</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>GC undetectable tars.</td>
<td>Biomass fragments, heaviest tars (pitch).</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Heterocyclic compounds. These are components that exhibit <strong>high water solubility</strong></td>
<td>Phenol, cresol, quinoline, pyridine.</td>
<td><em>Orange</em></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Aromatic components. Light hydrocarbons, which are important from the point view of tar reaction pathways, but not in particular towards condensation and solubility.</td>
<td>Toluene, xylems, ethyl benzene (excluding benzene.)</td>
<td><em>Orange</em></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Light poly-aromatic hydrocarbons (2-3) rings PAHs). These components condense at relatively high concentrations and intermediate temperatures.</td>
<td>Naphthalene, indene, biphenyl, antracene.</td>
<td><em>Orange</em></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Heavy poly-aromatic hydrocarbons (&gt;4-rings PAHs). These components condense at relatively high temperature at low concentrations.</td>
<td>Fluoranthene, pyrene, crysene.</td>
<td><em>Orange</em></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>GC detectable, not identified compounds.</td>
<td>Unknown</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Equilibrium tar concentration vs. dew point

Concentration $[g/m^3]$ vs. Temperature $[°C]$ graph showing the concentration of various compounds (Benzene, Phenol, Toluene, Fluorene, Pyrene, Naphthalene, Water, Anthracen) as a function of temperature. The graph illustrates the updraft, FBG, and downdraft conditions.
Questions, for a workshop on tar …

• What do we want to know with respect to tars in the produced gases from biomass gasification?
  – Just their condensation behavior (= issue) under certain process conditions \((P, T)\) dewpoint
  – Aromatic organic species distribution? From which threshold value?
    • Sampling ex- versus in-situ? frequency? On/off-line?
    • Detection frequency? On/off-line?

• Boundary conditions of Safety, Costs, Labor intensity …
Generic diagram for tar sampling & analysis

**Sampling point**

- **GAS**
  - Sampling point
  - **Off-line**
    - P.M. removal
    - **Accumulation**
      - Condensation
      - Adsorption (SPA)
      - Absorption/dissolution (**CEN/TS 15439**)
    - **Sample preparation**
      - Dilution, spiking (I.S.)
      - Desorption (thermal/solvent use)
      - Solvent evaporation
    - **Measurement/analysis**
      - GC/FID, GC/MS
      - HPLC
      - Gravimetric

- **On-line**
  - Measurement/analysis
    - Chromatographic separation (quasi-on-line)
    - **Excitation** (in-situ)
      - Molecule ionization & detection: PID, FID
      - Emission spectroscopy: LIF, UV
      - Absorption spectroscopy: UV/VIS, (FT)IR
      - Reflection measurement (TDA)
      - Mass selective: MBMS, TOF-MS, Ion-trap-MS, Quadrupole-MS

Adapted from Knoef et al., in Handbook Biomass Gasification 2nd edition 2012
When only condensation matters
Tar Dew Point analyzer (ECN) a possible solution

See www.thersites.nl
Another on-line tar analyser, based on tar condensation & FID detection: the OTA (IFK) Stuttgart / Ratfisch, DE

Different filter types and temperatures give global, total condensables indication relatively fast response time -> ‘dynamic’ measurements!

Presentation by Poboss (IFK, Stuttgart), European Biomass Conference 2011, Berlin
KTH – Novel tar analysis method based on on-line photo ionisation detection (PID)

Main Gas Components

Minor Gas Components

Contaminants

Tar components

8.4 eV
Light source

9.5 eV

10.2 eV

11.7 eV

Not detectable

Most likely detectable

Detectable

Source: http://www.evur.tu-berlin.de/menue/forschung/veranstaltungen/tar_workshop/
Presentation by Knoeff (BTG, Enschede) in cooperation with KTH, European Biomass Conference 2011, Berlin
Off-line techniques, existing

- Our benchmark so far: CEN/TS 15439
  - Current standard in Europe, thus well-defined, described, tested
  - Provides quality and quantity of heavy and light tars up to species level
    - Labor intensive -> costs
    - Slow regarding sampling AND analysis

Picture from CEN/TS 15439
Post-treatments

P.M. quantification

GC detectable tar species quantification

Lumped Heavy tar quantification

Picture adapted from CEN/TS 15439
Suitable Concepts - ‘derivatives’ from CEN / TS 15439

- **Filter**
- **Transferline**
- **1.Stage**
  - impinger 0°C
- **2.Stage**
  - -15°C
- **IPA**

**TU Vienna Approach**

- **Pre-cyclone**
- **Filter**
- **1.Stage**
  - impinger 10°C
- **2.Stage**
  - 0°C
- **Toluene**

- **BE/Graz since 2004**

- **Filter**
- **Transferline**
- **1.Stage**
  - Short column*)
  - 0°C
- **2.Stage**
  - -15°C
- **IPA, Methanol, Hexane**

- **PSI**

**Courtesy: Markus Kleinhappl (BE2020+)**
ECN setup for product gas sampling
(also suitable for water rich product gas)

CEN/TS: (7.1.2; page 12)

Nr 1: no frit;
nr 2: coarse/fine frit;
nr 3+5+6: medium/fine frit.
Only 1,2,3,4,5 filled with IPA
(Risk of plugging impinger 2 and 3)

ECN setup:
(no problem with high water content of product gas)

Nr 1 + 3: no frit;
nr 2+ 4+ 5: coarse frit;
nr 6: fine frit.
All impingers filled with IPA

Courtesy: Johan Kuipers (ECN)
Off-line techniques, existing

Solid Phase Adsorption

+ Simple, well-repeatable, fast sampling and elution
+ Samples can be well-preserved for higher, PAH tars
+ Quantification of species
- Slow analysis
- Detection limit might be on the high side

Pictures: courtesy ECN
Schematic from Brage et al. (1997), Fuel, 76 (2), pp.137-142
Comparison of SPA-NH2 with CEN/TS

(SPA samples were not stored in freezer for two days)

Ratio SPA / Guideline samples

Fluiddised bed gasification of RDF; febr. 2008

Courtesy: Johan Kuipers (ECN)
Intermediate Conclusions

• Using different setup of impingers/frits will help to prevent plugging of frits by fine particles/tar and plugging by ice crystals from condensed water.

• SPA-NH2 and CEN/TS results give comparable results for non-volatile tar components

• SPA-NH2 is not suitable for Benzene/Toluene (volatile); For Benzene/Toluene other SPA phase must be used or use (micro)-GC.
Adaptations to SPA

Series of spa standard tube with charcoal cartridge on top: Enhanced BTX sampling & analysis


Adaptations related to SPA (KTH)

Heavy tar sampler (left) and heated T-joint (right).

The T-joint allows simultaneous light tar analysis via septum (SPA) and connection to sampler for heavy tar analysis (by weight).

Included also: small gas flow meter and small gas pump.

Heavy tar + light tar = total tar

The method is in principle developed -> to be patented and/or published in near future.

Courtesy: Truls Liliedahl (KTH)
Laser Induced Fluorescence Spectroscopy (TUB/TUM)

+ In-situ
+ on-line
- Expensive
- Calibration complex, specialist needed

Source: http://www.evur.tu-berlin.de/menue/forschung/veranstaltungen/tar_workshop/
Presentations by TUM (Mayerhofer) and TUB (Zobel), European Biomass Conference 2011, Berlin
Comparison SPA with LIFS – TUD CFB steam – oxygen blown gasifier

Source: Meng et al. (2012) Fuel Processing Technology 100, pp. 16-29
Which items can be updated to CEN /TS?

**Improvement of definitions/declarations**

/ Type of Gas
/ Degree of Treatment

- Pyrolysis
- Types of Gasifiers
- Product gas for Engine
- Syngas conversion
- Fuel cells

/ discrete Components
/ families of compounds (=classes)
/ physically lumped classes

Methodology of Sampling ↔ Analysis ↔ Quality

Sampling
Analysis
Quality measures

/ Utilisation target
/ specific recommendations

- Burners
- Engines
- Syngas conversion
- Fuel cells

/ Cluster of quality parameters
Particulate/ Aerosol matter ‘tar’
‘tar-species’
Other
Include/exclude ASH

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**News:**
- Filter – elements /cross flow/ dilution methods
- Sampling probes (heated)
- Particles/aerosols/ classification of solids (T)
- Impingers ↔ columns ↔ cont. mass transfer

SOLVENT optimization??
- Liquid methods ↔ SPE (solid phase)

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**News:**
- Off-line / on-line
- Detection/Measurement
- HPLC/GC-methods
- Selective Recovery from SPE
- Hyper-systems with toolboxes®
- Water detection

- Test procedures of capture & analysis (testgas generators)