Tar analysis methods for small scale gasification systems

...from a KTH perspective...

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Outline

• Background
• Tar analysis in a small scale gasification system
  – Offline methods
    o “Conventional” tar analysis
    o Solid Phase Absorption (SPA)
    o SPME
  – Online methods
    o FID
    o PID
  – What is the conclusion?
• Summary
Background
Small scale gasification systems

Pretreatment
- Drying
- Grinding
- Sizing

Gasification
700-1000 °C

Gas cleaning
Removal:
- Particles
- Tars

CHP

Biomass

Air

High tar
(5-50 g/Nm³)

Low tar
Internal combustion engine: < 50 mg/Nm³
Gas turbines (directly fired): < 5 mg/Nm³
Challenge biomass gasification tars

- Production of condensable polyaromatic “tars” is inherent in most biomass gasification processes
- Tars foul and can plug equipment downstream of the gasifier
- Challenging to remove from the produced gas
- Reduce energy efficiency of gasification process
- Reports of as much as 10% of biomass carbon ending up in the form of tars
Challenge biomass gasification tars

Example internal combustion engine

Throttle valve tar deposits with water scrubbing (left), oil scrubbing (right)
What is tar?

The term "tar" is vague and the definition vary.

One definition is "organic molecules with a molecular weight higher than that of benzene" (Mw = 78 g/mol).
What is tar?

**Light tars**
Organic compounds that can be analysed with GC as well as HPLC. (Mw 79-300 g/mol). They are volatile and semi-volatile aromatics and phenolics.

**Heavy tar**
Organic compounds with so high boiling points that they can be analysed only by HPLC, not with GC. They are mixtures of high molecular weight "non-volatile" polar compounds (Mw \( \approx >300 \) g/mol)

Total tar = sum of light and heavy tar
What is tar?

Oxygenated compounds

Phenolic compounds and olefins

Polycyclic aromatic compounds
General scheme tar analysis

A few common steps:

1. **Sampling of the tar:** Generally collected from a side stream, including more or less complicated sampling equipment to attain a representative sample.

2. **Storage of sample:** Only valid for offline methods.

3. **Pre-preparation/conditioning of the sample:**
   - **Offline methods:** The collected tars are extracted to or dissolved in an appropriate solvent for further chemical analysis.
   - **Online measurements:** Conditioning such as drying of gas removal of particulates etc. may be required depending on the analytical technique.

4. **Analysis of sample:** Chemical analysis of pre-prepared/conditioned tar sample. Most common analytical techniques are based on gas chromatography (GC) or high pressure liquid chromatography (HPLC).
All these methods!

<table>
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<tr>
<th>Method</th>
<th>Development status</th>
<th>Application</th>
<th>Measured data</th>
<th>Offline/Online</th>
<th>Sampling and analysis time</th>
<th>Cost</th>
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<tr>
<td>Tar protocol/ guideline</td>
<td>CEN/TS pre-standard</td>
<td>Laboratory use</td>
<td>Gravimetric tar (Class 1) GC-FID (Class 2-5)</td>
<td>Offline</td>
<td>Long sampling and analysis time</td>
<td>Very expensive</td>
</tr>
<tr>
<td>Petersen column</td>
<td>Portable device</td>
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<td>Gravimetric tar (Class 1-5)</td>
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<td>Long sampling and analysis time</td>
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<tr>
<td>GC-FID and GC-MS</td>
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<td>Laboratory use</td>
<td>Individual tar compounds (Class 2-5)</td>
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<td>Short sampling time and relatively short analysis time</td>
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<tr>
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<td>SPA</td>
<td>Easy to use probe</td>
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<td>Individual tar compounds (Class 2-5)</td>
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<tr>
<td>SPME</td>
<td>Easy to use probe, Under development</td>
<td>Laboratory use</td>
<td>Individual tar compounds (Class 2-5)</td>
<td>Offline</td>
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<td>Online tar analyser]</td>
<td>Portable device</td>
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<td>Individual tar compounds (Class 2-5)</td>
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<tr>
<td>MBMS</td>
<td>Transportable</td>
<td>Industrial use</td>
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<tr>
<td>PID</td>
<td>Under development</td>
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<td>Low</td>
</tr>
<tr>
<td>Raman spectroscopy</td>
<td>Not transportable</td>
<td>Industrial use</td>
<td>Gravimetric tar (Class 1-5)</td>
<td>Online</td>
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</tbody>
</table>

- Large number of methods for tar measurement
- Generally:
  - For research and laboratory use
  - Complex – needs expertise
  - Several are expensive
  - Not robust enough process
  - ...
What method to use?

• Depends on information desired!
  - Qualitative or quantitative information?
  - Information about chemical composition?
  - R&D or industrial monitoring?
• Reliability?
• Costs?
• …
Requirements tar analysis small scale systems

Research
No real requirements
“A matter of need to know and costs!”

Industrial monitoring/analysis
• Reliable - high repeatability
• Low staffing
• No or low need for expertise
• Low costs
• Fast
• Tar composition generally not of interest
• Preferably online

Gasification
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Gas cleaning
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Air

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Tar analysis in a small scale gasification system
Offline methods

“Conventional” tar analysis

**Tar protocol** developed over several projects supported by IEA Bioenergy Task 33, US DOE and European Commission 1998-2005

- Significant contributions by ECN, VTT, KTH, DTI, BTG, NREL

Adopted as CEN standard for tar sampling

Offline methods

“Conventional” tar analysis

Procedure

• Draw specific volume of process gas through a filter and then a series of cold impingers to collect the tars

• Evaporate solvent to measure **gravimetric** (total) tars

• Analyze tars by **GC-MS** to evaluate composition

Quantitative, but very laborious
Offline methods

Solid Phase Adsorption (SPA)

- SPA sampling and analysis method was developed by KTH in the 1990’s.
- SPA used for measurement of the concentration (mass) of individual light aromatic hydrocarbons and phenols.
- The SPA-method is restricted to GC-available (GA) compounds only.
- These compounds are, however, significant process markers that provide good measures of reactor performance and gas quality.
- At $T = 900^\circ C$ and above the GA-compounds roughly correspond to the total tar amount.

Offline methods

Solid Phase Adsorption (SPA)

1 = to syringe or electrical pump; 2 = adapter (polypropylene); 3 = sample reservoir; 4 = sorbent tube (PP, 1.3 OD x 7.5 cm); 5 = fritted disc (20 mm polyethylene); 6 = amino-phase sorbent (40 mm, 60 Å); 7 = rubber/silicone septum; 8 = septum retainer (polypropene); 9 = “Tee”-adapter (glass); 10 = syringe needle (stainless steel); 11 = producer gas.

Solid Phase Extraction (SPE) - NH₂ tube
Offline methods

Solid Phase Adsorption (SPA)

Sampling
“T”, needle, SPE-NH$_2$ tube and 100 ml syringe.
Custom made reversible SPE tube.
Sampling of 100 ml in 1 min.

Sample storage
The SPE tube is capped in both ends after sampling.
Samples stored in a fridge/freezer.

Sample preparation
Elution for aromatic and phenolic compounds.

Chemical analysis
GC-FID - Gas chromatograph with flame ionisation detection.

Results
Detection limit: 2.5 mg/Nm$^3$ (for detectable tars)

Solid Phase Adsorption (SPA) with a temperature of 300°C. The SPA samples were analysed by a SHIMADZU QP5000 GCMS with a WCOT fused silica column. A typical chromatogram of the inlet tar is shown in Fig. 4. Several samples were taken at the same operating condition and the average value is presented here. Concentrations of individual tar compounds were calculated in mg m$^{-3}$ and then added to get the concentration of a particular tar class. The tar compounds that were considered for a particular class are tabulated in Table 1. Concentrations of compounds with a higher boiling point than pyrene were determined using the calibration data of pyrene. The heaviest compound identified was benzofluoranthene. Benzene is not considered as tar. Light tar, e.g. toluene, was identified, but could not be measured quantitatively accurately, especially at lower temperature. So toluene was not taken into account during total tar calculation, but presented separately. Very high molecular weight (class 1) tars and final gas composition could not be measured due to experimental limitations.

3.3. Catalyst characterisation

Two types of additives, olivine and dolomite were tested during these experiments. Calcined dolomite is a porous catalyst; its large (internal) surface area and the presence of oxides in its matrix (CaO, MgO) make it an active catalyst with respect to tar reduction. Olivine is a naturally occurring silicate mineral in which magnesium and iron are embedded in the silicate tetrahedral [10]. The properties of both the additives are tabulated in Table 3. The BET surface area has been measured by chemisorption with ASAP. Olivine is a nonporous material as it has an extremely low surface area. Results of mercury porosimetry for calcined dolomite are included in Table 3 as well, for olivine mercury porosimetry could not be done.
Offline methods

Challenges of SPA Method

- Inleakage of air, especially for sub-atmospheric pressure systems
- Using temperature high enough to avoid tar condensation yet low enough not to melt septum
- Plugging of needle by septum material
- Condensation of tars in needle of syringe
- Undesirable heating of SPE column during sampling due to temperature, steam condensation
- Breakthrough of light tars (BTX)
- Desorption of light components from SPE cartridge during storage
- Efficient elution of aromatic and phenolic compounds
- Inability to measure heaviest tars
- Consistency of procedures for sampling and analysis
## Offline methods

A (biased?) comparison between SPA and “Tar guideline”

<table>
<thead>
<tr>
<th>Cold solvent trapping (CST) (”Tar guideline”)</th>
<th>Traditional SPA (”KTH”)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Advantages:</strong></td>
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</tr>
<tr>
<td>- Gives total tar, heavy and light tar</td>
<td>- Uncomplicated and fast sampling</td>
</tr>
<tr>
<td><strong>Drawbacks:</strong></td>
<td>- Low cost</td>
</tr>
<tr>
<td>- Time consuming, sampling as well as analysis</td>
<td>- High accuracy and reproducibility</td>
</tr>
<tr>
<td>- Large solvent volumes</td>
<td>- Sampling and analysis can be done separately</td>
</tr>
<tr>
<td>- Not suitable for (very) low tar concentrations</td>
<td><strong>Drawbacks:</strong></td>
</tr>
<tr>
<td>- Low precision</td>
<td>- Not suitable for heavy tars</td>
</tr>
<tr>
<td></td>
<td>- B(TX) must be analysed within a few hours</td>
</tr>
</tbody>
</table>
Offline methods

SPA analysis at low tar concentrations and separate BTX analysis (KTH)

Determination of light tar in low concentrations

“A few other variants exists, e.g. Chalmers and ECN”
Offline methods

SPA analysis combined with gravimetric tar (KTH)

Heated and isolated “T”-connection with SPA-septa (left) and heavy tar sampler (right)

Sampler mounted on atmospheric fluidised bed gasifier
Offline methods

Solid Phase Micro Extraction (SPME)

**SPME device**

**Experimental set-up KTH**

- Method under development
- Extraction of analytes from a sample matrix onto a stationary phase (non-polar) - silica fibre with 50 µm polydimethylsiloxane (PDMS)
- Desorption of the analytes in an analytical instrument (GC)
- Developed for low tar content analysis in e.g. syngas applications
Offline methods

Solid Phase Micro Extraction (SPME)

- Tests on real gas with sampling time 10 min.
- The results showed that SPME method is a fast and accurate for low tar concentrations.
- Analysis at trace levels below 0.1 mg/Nm$^3$ (e.g., syngas production) will be possible at 60 °C for all compounds heavier than naphthalene.

Brisk report, Advanced measurement methods and operational procedures in thermochemical biomass conversion, D 7.6 Protocols/standards for tar measurement.
Online methods

Flame Ionization Detector (FID)

- Prototype developed by researcher at University of Stuttgart.
- The instrument is using FID as a the detector principle.
- The instrument can determine:
  - Total hydrocarbon concentration
  - The non-condensable hydrocarbon concentration
  - The tar concentration
Online methods

Flame Ionization Detector (FID)

**Measurement principle:**
Difference measurement of the organically bound carbon in the sample gas of two sample loops with equal volume.
Online methods

General impression:
• Easy to use
• Provide accurate results in comparison with "Tar protocol"
• The choice of a suitable tar filter material for the difference measurement was identified as one of the major challenges to gain realistic results.
Online methods

Photo Ionization Detector (PID)

"Method under development at KTH"

A molecule with an ionization potential (IP) lower than the actual energy \( E = h\nu \) of a photon is ionized.

\[
R + h\nu \rightarrow R^+ + e^-
\]

Energy required to remove an electron is different for each compound.

Typical tar compounds require relatively little energy.

Possibly a selectivity can be achieved.
Online methods

Photo Ionization Detector (PID)

Energy of the light depends on the gas inside the lamp
Xenon = 8.4 eV
Aromatic compounds with IP < 8.4 eV can be detected, e.g.:
- Naphthalene
- Acenaphthene
- Flourene
- Anthracene
- Pyrene

Not detectable
Detectable

(eV)
Online methods

Photo Ionization Detector (PID)

**PID in a real gas stream**

Schematics of the tar measurement system for real gas tests at BTG

Online methods

Photo Ionization Detector (PID)

**PID in a real gas stream**

- The PID signal follows the SPA signal at almost all different tar levels.
- Both real gas and naphthalene PID signal shows a linear correlation comparing with SPA tar content.
Some observations:

- Different response curves of the compounds will make quantification less accurate during analysis of real producer gas
- Fouling of UV lamp window with time is an issue.
- PID prototype test system developed to address the window fouling problem
- Prototype tests in progress
What is the conclusion?

Biomass → Gasifier → Gas cleaning for CHP → Or → Gas cleaning for fuel cell, other?

- **High tar** (10-50 g/Nm³)
  - Offline: SPA, Tar protocol
  - Online: PID, FID
- **Medium tar level** (5-50 mg/Nm³)
  - Offline: SPA, Tar protocol
  - Online: PID, FID
- **Low tar**
  - Below dew point: 0.1 mg/Nm³ at 100 °C
  - Offline: SPME
  - No viable technique
Summary
Summary

• Simple, low-cost, yet robust means of measuring and characterizing tars is desirable, especially for small scale systems
• Impinger-based method of standard tar protocol is relatively robust but time consuming and laborious
• SPA method much simpler and equally as good for many situations, but does have drawbacks
• Continued development of SPA procedure will improve robustness and utility of the method
• Developed FID and PID under development are both promising candidates for future industrial online tar monitoring
Thank you!

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