Tar & (SPA) tar analysis

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Tar when gasifying biomass

Gasification at 700-800 °C typically gives a condensable fraction (tar) consisting of phenols and aromatic hydrocarbons covering a wide range of molecular weights. As soon as the temperature drops below the tar dew point, the tars will either form aerosols or condense directly on the inner surfaces of the equipment, resulting in plugging and fouling of pipes. Tars may also undergo dehydration reactions to form solid char and coke that further plug up the system.

The term "tar" is vague. One definition is "organic molecules with a molecular weight higher than that of benzene" (Mw 78).

Tar definitions

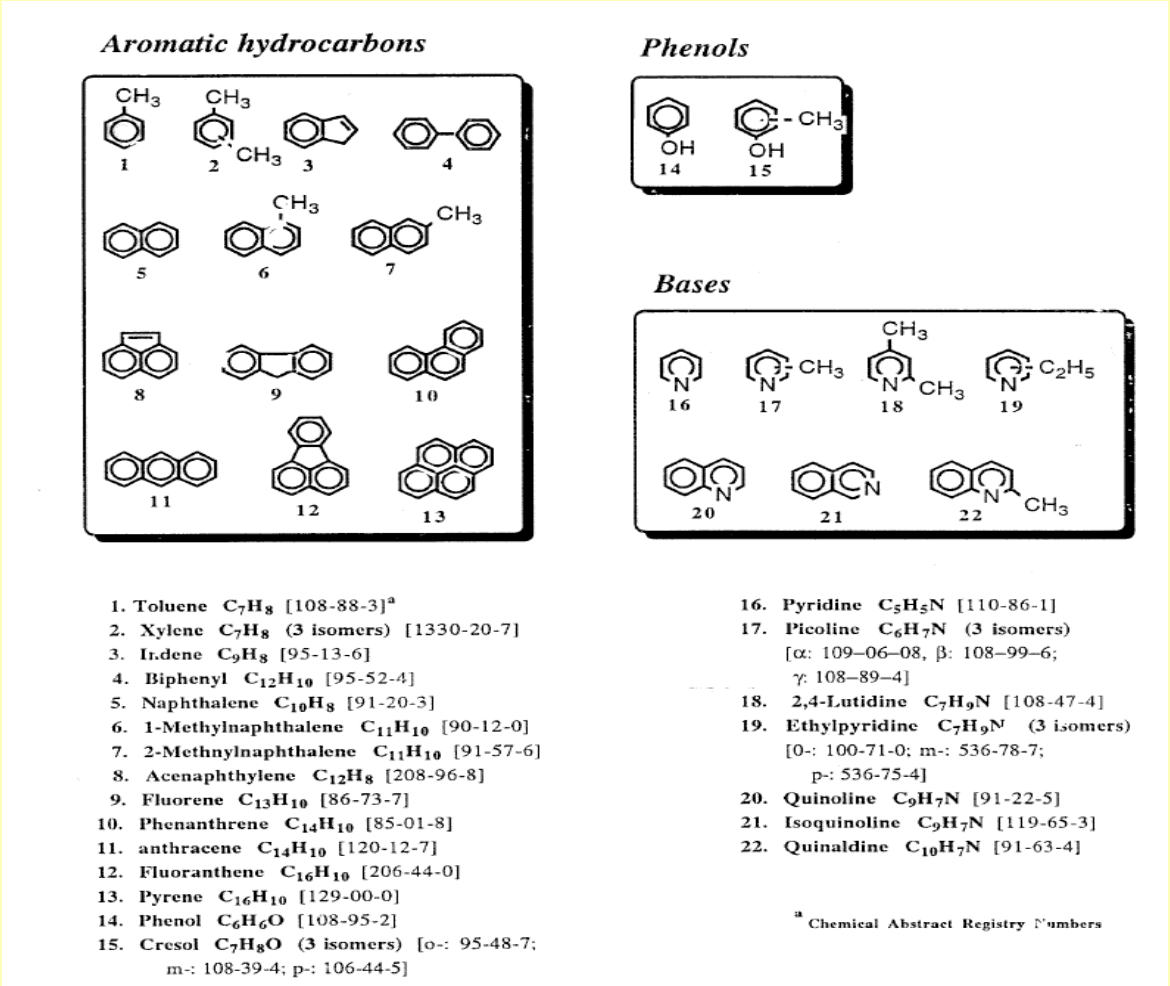
Light tars = organic compounds that can be analysed with GC as well as HPLC. (Mw 79-300). They are volatile and semi-volatile aromatics and phenolics.

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 ≈>300)

Total tar = sum of light and heavy tar

Three generic tar compound groups may be found

Generic Principle:
No phenols ➔ No heavy tar



Sampling and analysis principles for tar analysis

Cold-solvent-trapping, CST[1]: ≈ 100-1000 litres of a gas is passed through a series of impingers containing a ice-cooled solvent. After preparation, samples are subjected to GC to measure individual compounds and gravimetry for total tar.

Solid-phase adsorption, SPA[2]: ≈ 100 ml producer gas is passed through a disposable cartridge containing 500 mg of amino-phase (modified silica). After preparation, samples are analysed for individual compounds by GC.

On-line tar analyser[3]: The method is based on the comparison of the total hydrocarbon content of the hot gas and that of the gas with all tars removed. Hot gas from the gasifier is led directly into the set up. Hydrocarbons are measured with a flame ionisation detector (FID).

[1] CEN/TS 15439 Biomass gasification –Tar and particles in product gases - Sampling and analysis (May 2006).

[2] Brage, C.; Yu, Q.; Chen, G,; Sjöström, K.; Fuel Vol.76, No. 2, pp. 137-142, 1997.

[3] Moersch, O.; Spliethoff, H.; Hein, K.R.G. ; Biomass and Bioenergy 18 (2000) 79-86

Drawbacks of principles

CST: Long sampling time, laborious and time consuming sample preparation. Not useful for minute-by-minute monitoring. Exhibits a large operator dependence and is thus relatively inaccurate.

SPA: Can not be used for heavy tar measurements. BTX analysis can be problematic.

On-line analyser: Expensive and poorly documented. Not useful for measurement of individual compounds and low tar concentrations.

Solid-Phase Adsorption (SPA) for analysis of light biomass tar

The SPA-method is restricted to GC-available (GA) compounds only. However, these compounds are significant process markers that provide good measures of reactor performance and gas quality.

At 850-900°C and above do the GA-compounds roughly correspond to the total tar amount.

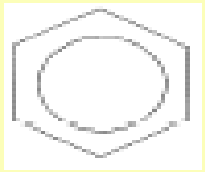
SPA, cont

SPA is used for the measurement of the concentration (mass) of individual light aromatic hydrocarbons and phenols. The method is used for the measurement of the concentration of individual light aromatic hydrocarbons and phenols. The method involves trapping of tar vapours on to aminopropyl-bonded silica packed in a small polypropene cartridge. Analytes are desorbed by two different eluents and the fractions analysed by gas chromatography (GC) with flame ionisation detection (FID). Following the "like adsorbs like" principle, phenolic compounds are more strongly held on this polar phase than the aromatic compounds.

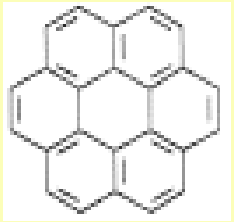
For the aromates and phenolics, repeatability for GC-analysis is less than 1%; repeatability and reproducibility of the method, random errors (sampling, sample preparation and GC-analysis) is typically ±5%. Larger deviation may occur for unknown analytes if the background is high (many small peaks slightly above the FID background signal).

SPA, cont

Through traditional SPA may compounds ranging in molecular weight from 78 (benzene) to 300 (coronene) be determined.



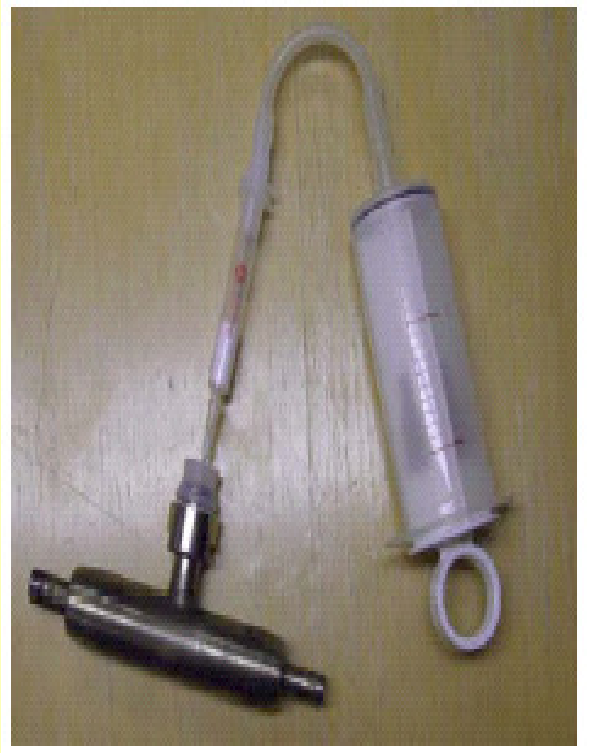
Benzene



Coronene

Internal standards for the quantitative analysis are TBCH [tert-butylcyclohexane] and PEP [p-etoxyphenol]. Derivatisation of the phenolic fraction is for improving the chromatographic performance. The method is normaly calibrated for 18 aromatics and 10 phenolics. However, this range can be extended if necessary.

SPA sampling, cont

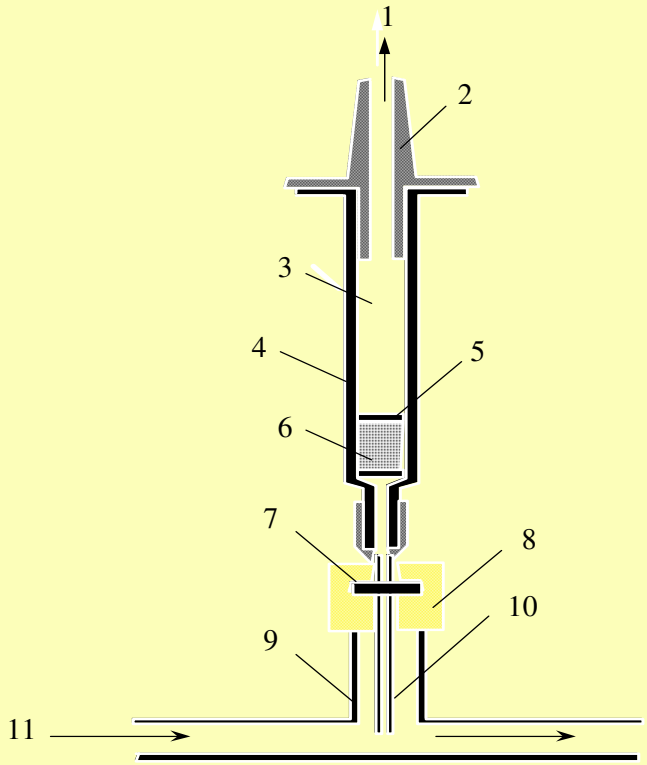


"T", needle, SPE-NH2 tube and syringe 100ml.

The SPE tube is capped in both ends after sampling.

Custom made reversible SPE tube, it consists of a female Luer inlet and a Luer male outlet.

SPA sampling



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

SPA sampling

For improved BTX-analysis should the GC-analysis be done the same day as the sampling and the cartridge should be caped directly after sampling, preferably with Supelco caps.

Kwik-draw

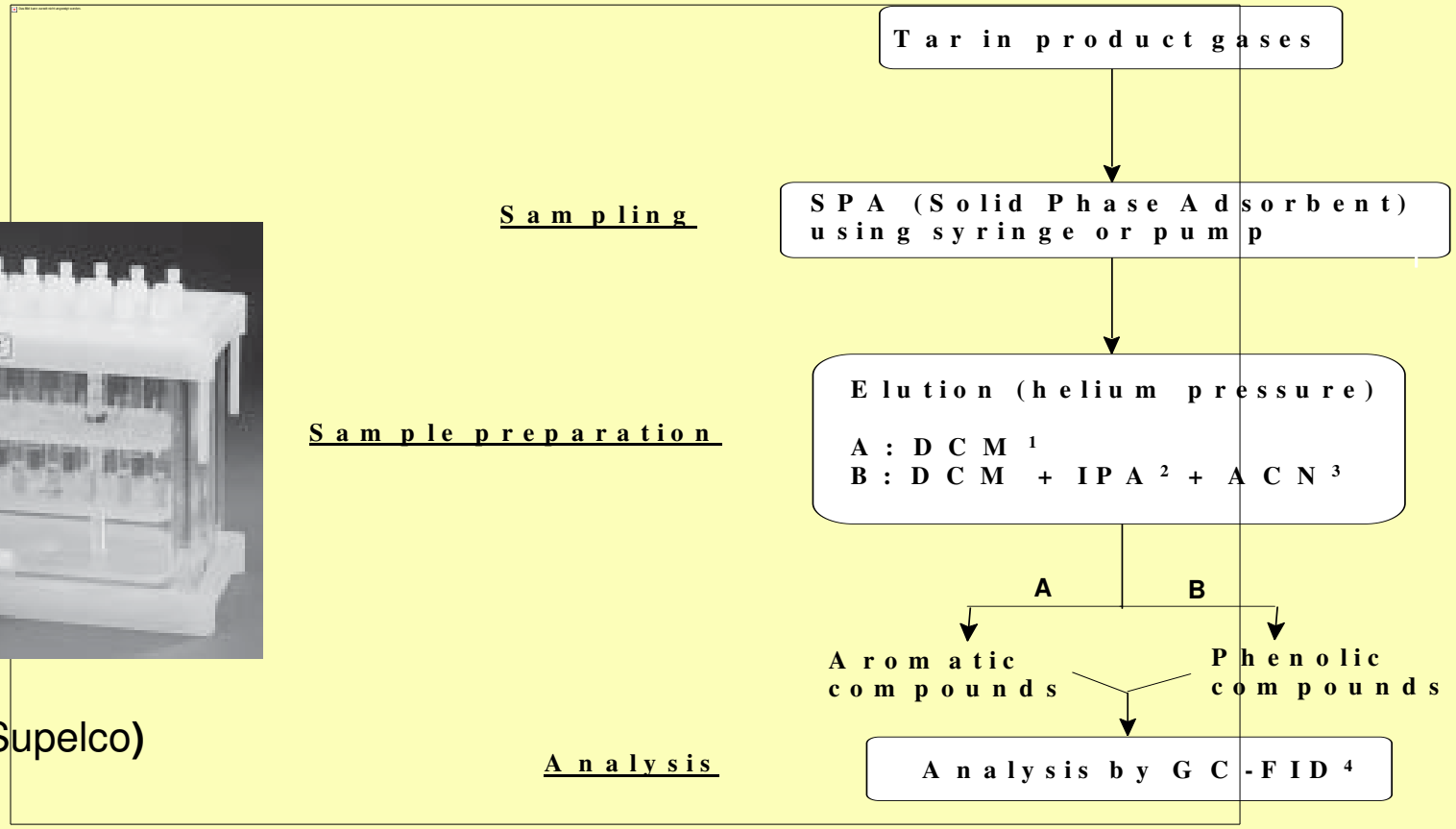
SPA is not a standard, more a principle, thus is it flexible and should be adapted to the given circumstances.

A Kwik-draw pump can replace the syringe.

SPA sample upgrading and analysis

Analysis Scheme for Gasification Tar

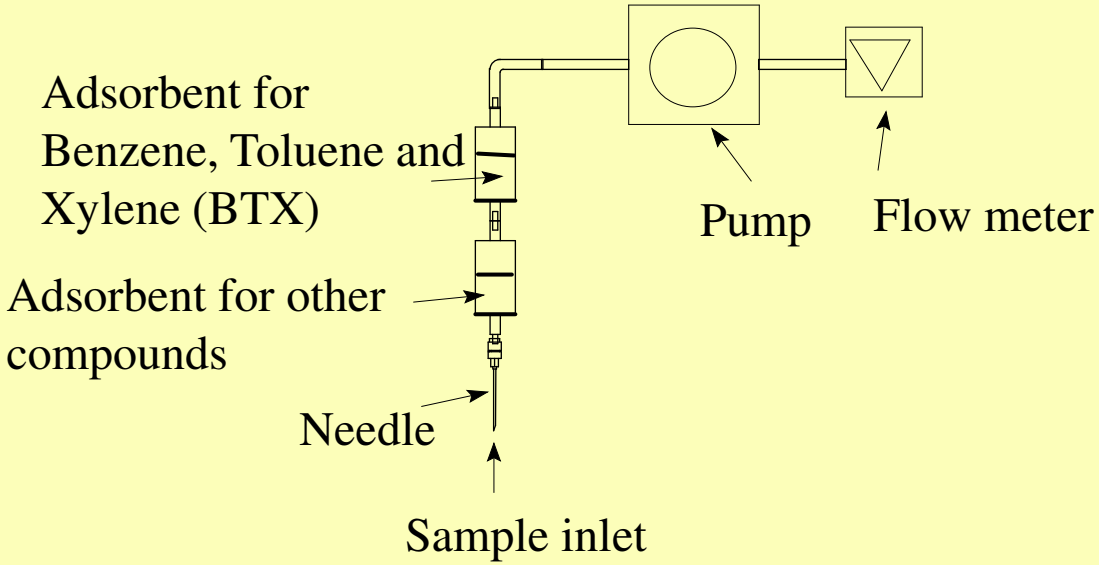
VISIPREP (Supelco)



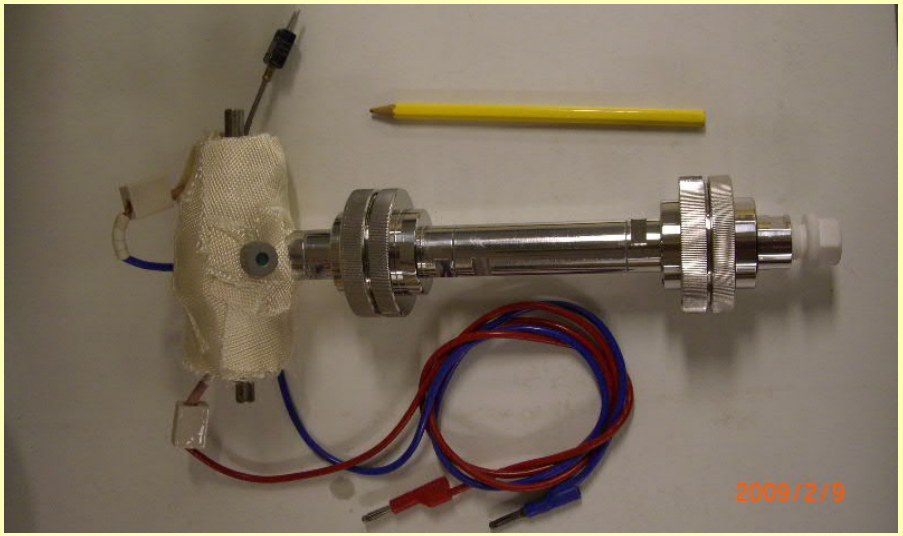
[1] DCM = dichloromethane
[2] IPA = isopropanol
[3] ACN = acetonitrile
[4] GC-FID = gas chromatography with flame ionisation detection

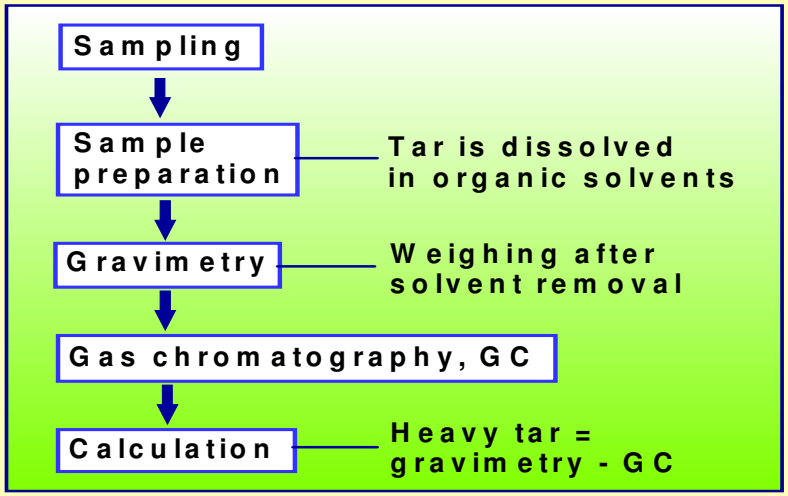
SPA sampling at low tar concentrations and separate BTX analysis

Determination of light tar in low concentrations



New method for analysis of total tar





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