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DTBH - Laboratoire des Technologies de la Biomasse

A promising new on-line method of tar quantification by mass spectrometry during steam gasification of biomass

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In biomass gasification processes pollutants may induce:

- Saturation of the gas cleaning systems
- Degradation of the catalysts used for fuel synthesis

→ Online method necessary to detect variation of pollutants
→ Sensitivity requirement: ppbv level after gas cleaning

Existing on line measurements methods for Tar

BTX → µGC-TCD [Ravel, 2010]
PAH → LIF [Sun, 2010], [Baumhalk, 2011], [Meng, 2012]
BTX PAH alkalis …→ MBMS [Carpenter, 2007]
Pyrolysis gas → SPI or REMPI TOFMS [Fendt, 2012]
Total tar contents
→ Tar Dew Point ECN [Rabou, 2009]
→ FID TA 120-3 IFK U. of Stuttgart [Poboss, 2011]
→ PID [Ahmadi, 2012]

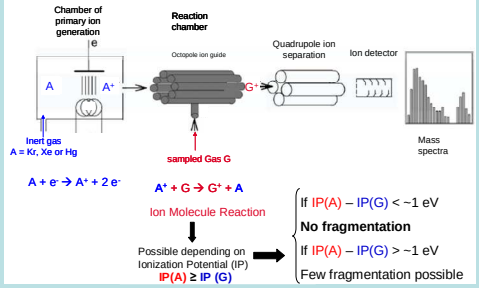
Drawback of these methods:

- Several methods to cover all tar and all content level
- Numerous fragmentations with electron impact ionization
- Only identification and no quantification
- Strong overlaps
- Nature of the species is not known

Objectif of this study: Present an on line mass spectrometry method tested successfully on real syngas for tars

IMR-MS principle

IMR-MS → Chemical Ionization with ionized inert gas (Xe, Kr, Hg) instead of CH_4, NH_3…



$A + e^- \rightarrow A^+ + 2\,e^-$

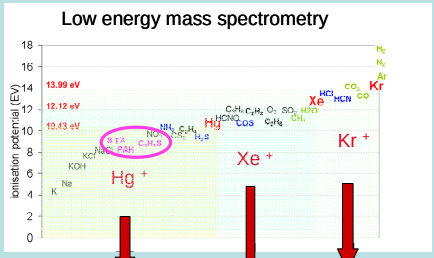
$A^+ + G \rightarrow G^+ + A$

Ion Molecule Reaction

Possible depending on Ionization Potential (IP)
IP(A) ≥ IP (G)

If IP(A) – IP(G) < ~1 eV
No fragmentation
If IP(A) – IP(G) > ~1 eV
Few fragmentation possible

Low energy mass spectrometry



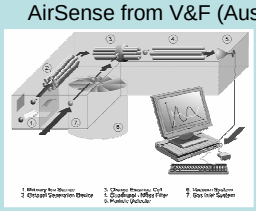
Best case :
BTX PAH C_2H_5S
Also NH_3 H_2S C_2H_4

Also HCN HCl CO CO_2
But overlapping possible with Hg^+ and Xe^+ species

Also COS C_2H_2 C_2H_4 CH_4 H_2O
But overlapping possible with Hg^+ species

IMR-MS Apparatus

AirSense from V&F (Austria)



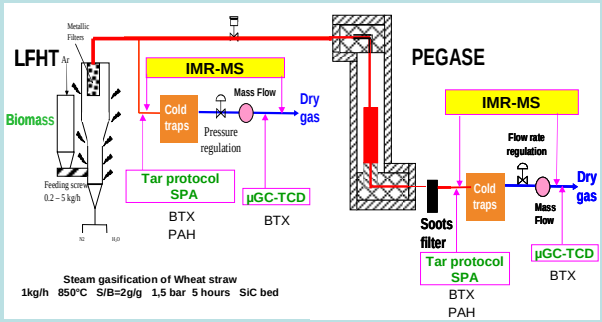
Mass range : 0 – 500 amu
Very fast answer: ~ 1ms per mass
Measuring range: from ppbv to %v
Linear response for calibration

Very compact (59x65x73cm)
Easy to carry 100kg (wheels)

Suitable for hot wet gas (above steam and tar Dew Point)
- Low pressure capillary sample gas heated (180°C)
- Neutral dilution

Biomass gasification Test

Concentrated tars | Bubbling fluidized bed | Tar cracker at 1400°C | Trace tars



Steam gasification of Wheat straw
1kg/h 850°C S/B=2g/g 1,5 bar 5 hours SiC bed

IMR-MS software

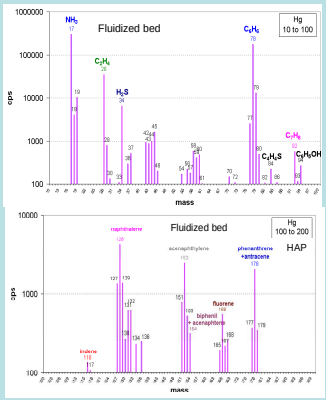
Two modes:

1- monitoring mode (more than 20 ions at the same time for 3 inert ions)
2- scan mode → mass spectra for each inert ion

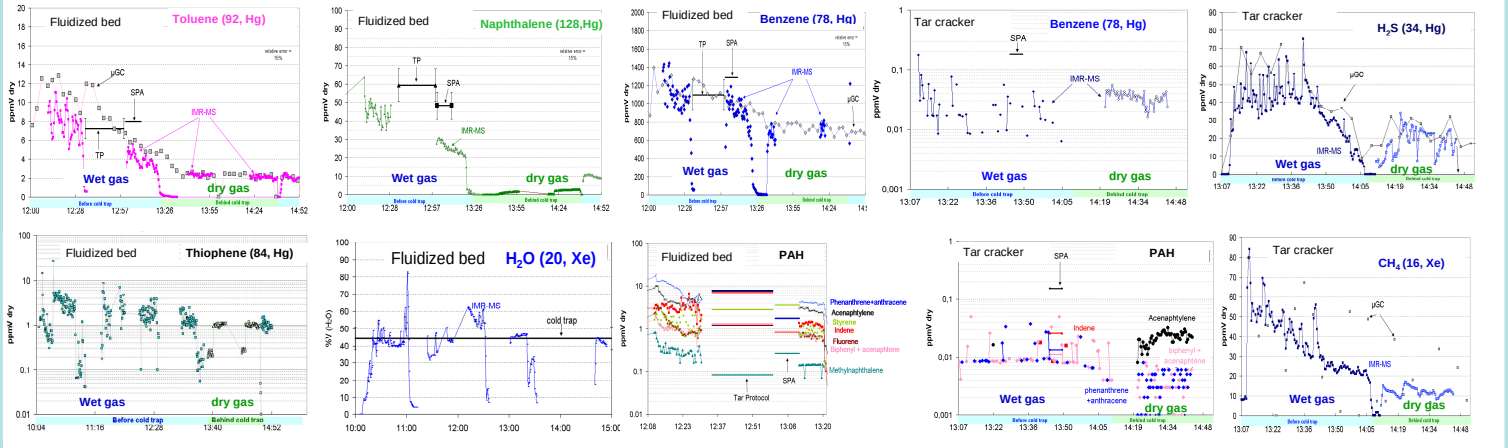
IMR-MS calibration

- Done for BTX + inorganics and some major gas
- Not done for PAH and thiophene

IMR-MS Mass spectra



IMR-MS results



CONCLUSIONS :

First time IMR-MS is tested to measure tars of a real syngas
- BTX and PAH (high and trace content)
- Thiophene detected easily
- On wet gas or dry gas

Good confidence of the IMR-MS results
Comparison with µGC-TCD, SPA + TD-GC-FID, TP + GC-FID

Potential for process control monitoring as well as research and development applications

Improvements
- PAH and thiophene calibration
- Measure inorganic pollutants as H_2S COS NH_3 HCN HCl (take into account overlap)
- Measure major gas as CO CO_2 H_2O CH_4 C_2H_n
- Build a fragmentation database at such low ionization potential

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