NEW METHODS AND DEVELOPMENTS ON SYNGAS POLLUTANTS ANALYSIS

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The development of renewable energy is a major topic all over the world, in response to various environmental, geopolitical and economic issues.

Biomass thermochemical conversion is a promising way to make renewable energy. The R&D GAYA project supported by ADEME* aims to develop at an industrial level the 2nd generation biomethane pathway trough biomass gasification and methanation.

Some developments need to be achieved before reaching industrial scale for this innovative renewable pathway.

The Research Center of GDF SUEZ (CRIGEN, Gas Quality Section) in collaboration with the CEA – LITEN, investigates many technologies of gas sampling and analysis applied to syngas characterization.

** French Environment and Energy Management Agency*

MAIN GASES

- Carbon monoxide(CO)
- Hydrogen (H_2)
- Methane (CH_4)
- Carbon dioxide (CO_2)

ORGANIC COMPOUNDS

naphtalene

- Polynuclear Aromatic Hydrocarbons (PAHs)
- Volatil organic compounds (VOCs): BTEX, styrene, phenols and derivatives…
- Thiophene, pyridine

SYNGAS

Temperature, pressure, moisture, dust

INORGANIC COMPOUNDS

- Ammonia (NH_3)
- Hydrogen sulfide (H_2S)
- Carbonyl sulfide (COS)
- Hydrogen chloride (HCl)

phenol

Figure 1: Syngas composition

SCOPE

All along the biomass gasification/ methanation process, **gas sampling and analysis constitute key steps** in order to:

- Characterize and control the syngas quality (Figure 1)
- Adjust and optimize the different process parameters

Investigations related in this study are targeted tars and inorganic compounds (sulphurs, ammonia...)

New sampling and analytical methods are investigated to characterize and quantify them.

STRATEGIES

Different strategies were tested to measure tars and inorganic compounds.

- **On-line measurement**: µGC-TCD** (Figure 2)
- **Off-line methodology**: gas sample pre-concentration step by Tar Protocol or solid phase adsorption SPA (Figures 3 and 4) + GC-MS** or HPLC- DAD/FLD** or ionic chromatography analysis.

***µGC-TCD: micro-Gas Phase Chromatography coupled to Thermal Conductivity Detector*
GC-MS: Gas Phase Chromatography coupled to Mass Spectrometry
HPLC-DAD/FLD: High Performance Liquid Phase Chromatography coupled to a UV Diode Array Detector or to a Fluorescence Dectector

Figure 2: µGC-TCD (Agilent and SRA)

Figure 3: Tar Protocol

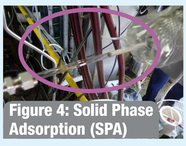


Figure 4: Solid Phase Adsorption (SPA)

PROMISING FIRST RESULTS:

- The use of GC-MS off-line technology after SPA gas sampling allows the **identification** of more than 50 organic compounds **(HAP, BTEX, Phenols, Thiophene and others…)** and the **quantification** of nearly 20 of them (Figure 5)
- On-line technology via µGC-TCD permits efficiently the measurement of **low mass tars** (i.e. BTEX) contained in syngas (Figure 6)
- The **quality of the CRIGEN measurements** was confirmed by the good match with the CEA ones (Figure 6)
- **H_2S** study is well initiated: quantification possible by µGC-TCD till 3 ppm concentration range. More investigations with others technologies are necessary to reach lower concentrations.

Figure 5: Correlation between CRIGEN and CEA Studies of Benzene and Toluene Concentrations

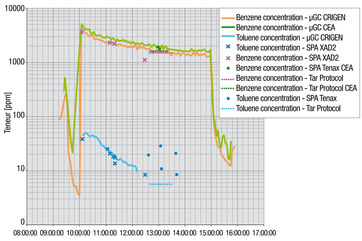
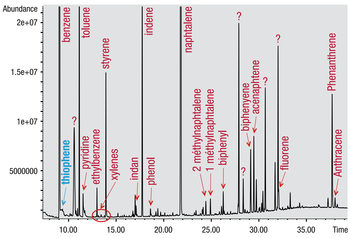


Figure 6: GC-MS chromatogram of syngas analysis (sampling by SPA)



These results allow good outlooks for monitoring 2G biomethane production

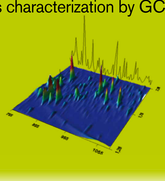
Analytical developments have to be continued through 3 axes…

ASSESSMENT OF NEW ON-LINE TECHNOLOGIES

- Measurement of heavy tars with mass spectrometer, (e.g. IMR-MS***, Airsense)
- Measurement of low concentrations of inorganic compounds by adsorption spectroscopy (e.g. OFCEAS***, Proceas)

DEVELOPMENT OF NEW ANALYTICAL METHODS

- Quantification of phenol and derivatives by HPLC-DAD/FLD
- Syngas characterization by GCxGC-MS***



OPTIMIZATION OF GAS SAMPLING PROTOCOLS

- Thiophene pre-concentration by SPA
- Low concentration range of tars by SPA

**** IMR-MS: Ion Molecular Reaction-Mass Spectrometry*
OFCEAS: Optical Feedback Cavity Enhanced Absorp- tion Spectroscopy
GCxGC-MS: comprehensive two-dimensional gas chromatography coupled to Mass Spectrometry

CEA is gratefully acknowledged by providing syngas from their high temperature fluidized bed reactor.