RICE
Research & Innovation Center for Energy

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Characterization by TD-GCxGC-ToFMS of Volatile Organic Impurities in raw renewable gases produced by Pyrogasification

Context & Objectives

To achieve the objectives of **renewable gases** content **in the gas grids** (10% in 2030 and up to 100% in 2050 in France [1]), innovative processes such as pyrogasification and methanation are studied in R&D pilots.

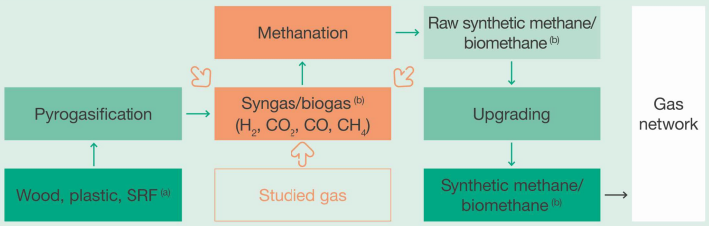
Pyrogasification consists in heating solids such as biomass or Solid Recovered Fuel (SRF) at high temperatures from 600 to 900°C. Methanation is the final step in the process of forming synthetic methane.

Yet, **the detailed composition of the produced gas is far from being well known** because focus is generally put on the analysis of major components. A better knowledge in the detailed composition of the produced gas is mandatory to **adapt the purification steps.**

The present study aims at characterizing **traces of organic compounds** in the raw syngas produced by pyrogasification and in the syngas after one step of purification by **direct thermal desorption GCxGC-TOFMS** [2,3].

Experiments were performed on raw gases with potentially higher levels of trace compounds in order to optimize the sampling process and the analytical method. Once the optimization achieved, these processes will be applied on purified gas.

Gas from waste by pyrogasification: main steps



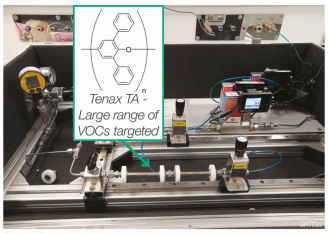
(a) Solid Recovered Fuel
(b) Decree of 30/09/2021 => Biogas = fuels or gaseous fuels produced from biomass

Source: GRTGaz

Material & Methods

Gas sampling

- On site
- Samples collected in a portable vessel (Tenax® Tube)
- Controlled flow rate
- Representative of the gas collected

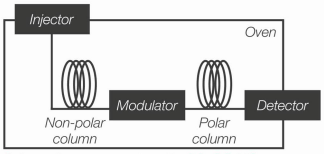


Sampling system

TD-GCxGC-ToFMS

Tubes collected on site were desorbed with thermal desorption unit into chromatographic apparatus. Comprehensive two-dimensional gas chromatography coupled with Time of Flight Mass Spectrometer was used.

- 1D: column of usual dimensions, separation in tenths of a minute
- 2D: very short column (≈1m), separation in seconds
- Nitrogen cryogenic modulation

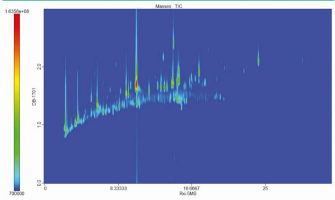


Schematic representation of a GCxGC-MS

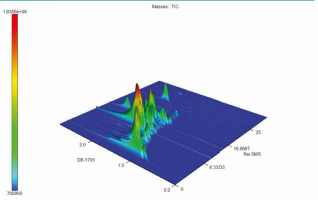
Analysis performed on a LECO Pegasus BT4D system and a Markes TD100-xr

Qualitative results

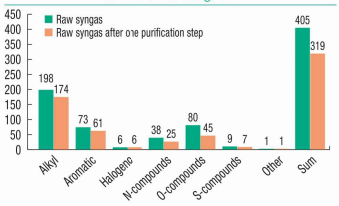
Chromatogram (2D Color plot) from a raw syngas analysis, Column 1D: Rxi-5MS, 2D: DB-1701



3D representation of the GCxGC chromatogram



Spatial organization of compounds by family on the chromatogram



- Bar chart representing the number of compounds identified per family of compounds in raw syngas and after one step of purification.
- More than 400 compounds were identified at trace levels (≈mg/Nm³) with the TD-GCxGC-ToFMS method. A similar number of compounds has been observed in biomethane from methanisation injection into the gas grid using a TD-GC-MS method.

Quantitative results

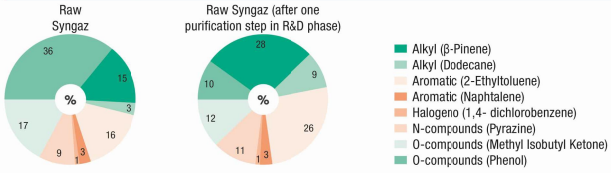
Hundreds of compounds were identified at trace level: individual quantification impossible

- Quantification by equivalent: compounds were classified by family; a reference compound for each family was chosen

Examples of reference compounds (family in parentheses)

Dodecane (Alkanes)		β-Pinene (Alkenes & Alkynes)		Pyrazine (N-Compounds)		2-Ethyltoluene (Aromatic)	
Naphtalene (Aromatic)		Methyl Isobutyl Ketone (MIBK) (O-Compounds)		Phenol (O-Compounds)			

Pie charts representing the composition by family in raw syngas and after one step of purification



Conclusions & Perspectives

Conclusions

- TD-GCxGC-ToFMS: method of choice for the analysis of VOCs of renewable gases.
- More compounds identified in GCxGC-MS compared to GC-MS (160 vs 500): GCxGC-MS allowed to overcome co-elution encountered with GC-MS.
- Useful information to choose the adequate purification process in the production chain to obtain gases suitable for injection into the gas grids.

Perspectives

- Upcoming field campaigns to characterize gases from different processes supplied with different inputs.
- Application of the optimized analytical method to purified gas injected into the gas grids and evaluation of the potential impacts of detected compounds on the gas grids.
- Establishment of technical specifications to regulate the injection of purified gases in the gas infrastructures.

References: [1] A 100% Renewable Gas Mix in 2050?, Study summary; ADEME, (2018) | [2] Hilaire, F.; Vial, J.; Thiebaut, D. *Apport de la chromatographie bidimensionnelle en phase gazeuse dans la caractérisation fine et l'interprétation des spécificités d'un biogaz et d'un biomethane ;* Étude RECORD N° 15-0155/1A; 2016 | [3] Hilaire, F.; Basset, E. Bayard, R.; Gallardo, M.; Thiebaut, D.; Vial, J. Comprehensive Two-Dimensional Gas Chromatography for Biogas and Biomethane Analysis. *Journal of Chromatography A* 2017, 1524, 222–232

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