GERG Biomethane project – Biomethane trace components and their potential impact on European gas industry

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Marine JUGE

Summary

Biomethane quality in Europe

Biomethane standards:

- **EN 16723-1**: Natural gas and biomethane for use in transport and biomethane for injection in the natural gas network - Part 1 : specifications for biomethane for injection in the natural gas network → **systematic review in Nov 2021**
- **EN 16723-2**: Natural gas and biomethane for use in transport and biomethane for injection in the natural gas network - Part 2 : automotive fuels specification → **systematic review in June 2022**

… some parameter in EN 16726: Gas infrastructure - Quality of gas - Group H (systematic review in Decembre 2020)

Depends on the substrate used in methanisation units, biomethane quality can change

→ Trace compounds: siloxanes, H_2S, O_2 …

Parameter	Unit	Limit values[a]		Test method (informative)
		Min	Max	
Total volatile silicon (as Si)	mgSi/m³		0,3[b]	EN ISO 16017-1:2000 TDS-GC-MS
Hydrogen	% mol/mol	-	2	EN ISO 6974-3 EN ISO 6974-6 EN ISO 6975
Hydrocarbon dew point temperature (from 0,1 to 7 MPa absolute pressure)	°C	-	−2 (as in EN 16726)	ISO 23874 ISO/TR 11150 ISO/TR 12148
Oxygen	% mol/mol	-	1	EN ISO 6974- series EN ISO 6975
Hydrogen sulfide + Carbonyl sulfide (as sulfur)	mg/m³	-	5 (as in EN 16726)	EN ISO 6326-1 EN ISO 6326-3 EN ISO 19739
S total (including odorization)	mgS/m³		30[c]	EN ISO 6326-5 EN ISO 19739
Methane Number	Index	65[d] (as in EN 16726)		Annex A of EN 16726:2015
Compressor oil			[e]	ISO 8573-2
Dust impurities			[e, f]	ISO 8573-4
Amine	mg/m³		10	VDI 2467 Blatt 2:1991-08

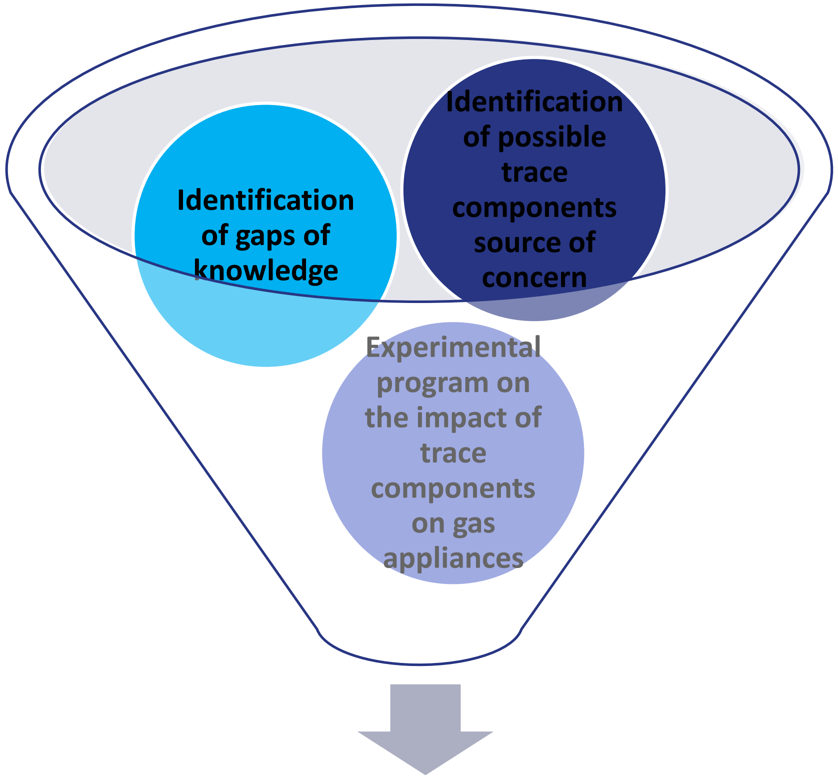
Biomethane injection into the natural gas grid should respect standard EN 16723-1

Towards the removing of technical barriers to biomethane injection into the natural gas grids

Standards revision of EN 16723 1 et 2 are performed in the GERG project with European gas actors

Gas operators work with GERG about their common worries about biomethane

European Commission (CEN TC 408) priorities are also considered in the work program of the project



SHARE DATA WITH THE BIOMETHANE INDUSTRY STAKOLDERS FOR FUTURE REVISION OF THE STANDARDS

The overall objective of the project is to offer the conditions to a **safe** development and a **competitive** positioning of the biomethane chain on the market

➔Have objective data to assess the real impacts of bioCH_4 specific trace compounds

➔Review the standards

…Keeping in mind the unavoidable economic aspects

Biomethane trace components and their potential impact on European gas industry

Towards the removing of technical barriers to biomethane injection into the natural gas grids

A multi-phase project aiming to revise the standards limits regarding trace component in biomethane

Phase 1

GERG gas industry priorities: Status review and gap analysis:

- Siloxanes
- Corrosive components
- Micro-organisms

January 2018

Phase 2a:

Combination of GERG priorities & CEN immediate priorities:

- Status review and gap analysis
  - Sulfur
  - Oxygen
  - Health impact assessment
- Experimental program: impact of siloxane on:
  - Industrial boilers
  - Heavy duty vehicles performance

SA/CEN/RESEARCH/475/2017-07

November 2019

Phases 2b & 2c

Follow up from Phases 1 & 2a + new proposals

WP1: Experimental program on siloxanes impacts

- Boilers: cycling mode (start and stop)
- Engines: test on switching type oxygen sensors

WP2: Experimental program on the impact of sulfur on vehicles After Treatment System (Catalysts)

WP3: Experimental program on the impact of oxygen and corrosive components on gas facilities:

- Gas grid
- Underground Gas Storage

WP4: Improve knowledge on biomethane

- Biomethane quality database
- BioSNG & bioLNG quality data
- Odor masking impacts
- Terpenes impacts

GERG Project Phase 2a results

SA/CEN/RESEARCH/475/2017-07

WP 1: Siloxane impacts

Siloxane impact on industrial boilers

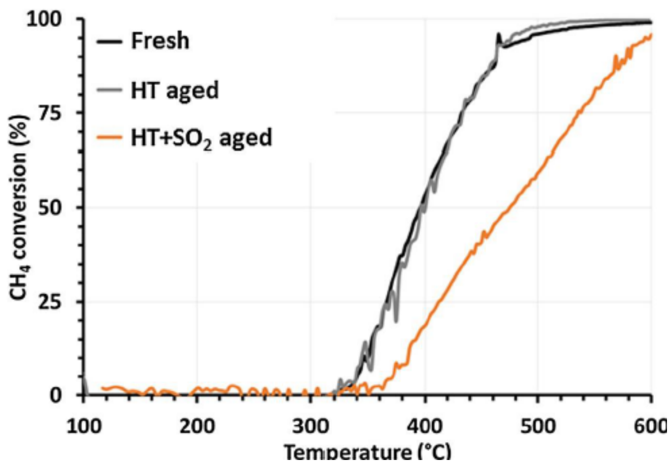
- No failure of the boiler = no weakening of heat transfer
- Silica deposition has been observed on the smoke tubes and reversal chamber
- The silica deposition on ionization probe led to a large decrease of ionization signal
- silica particles that coalesce to bigger particles which in turn abraded the refractory material of the reversal chamber

Siloxane impact on heavy duty vehicles

- Silica deposition on the spark plugs but no failure has been observed as well as no indication of misfire
- The engine efficiency has only changed marginally after the running 1005 hours with siloxanes in the fuel
- Two oxygen sensors have been subject to a strong silica deposition that led to the failure of one of them
- Silica deposition has been observed on different part of the engine but with no real impact on its performances

WP 2: Sulphur impacts

- **Literature survey on sulphur impact on ATS systems**
  - The presence of sulphur in biomethane (mainly H_2S) can lead to failure of the catalyst
  - After combustion, sulfur is oxidized into SOx species
- **Principal conclusions**
  - Sulphur does not poison the catalyst but rather facilitate the poisoning by water
    - Sulfur stabilize structural O_2
    - H_2O stabilize the inactive $Pd(OH)_2$
  - Deactivation rate of the catalyst seems to be dependent on the SO_2 concentration
  - Even very small amount of sulfur can cause rapid deactivation of the catalyst
  - Efficient catalyst regeneration can be achieved thanks to sulfates decomposition and SO_2 desorption
    - Exemple : In fuel rich conditions, combined with temperature above 500°C



Perform an experimental program on both light and heavy-duty vehicle with different total sulphur concentration is necessary to proposed a concentration limit to be implemented in the standard

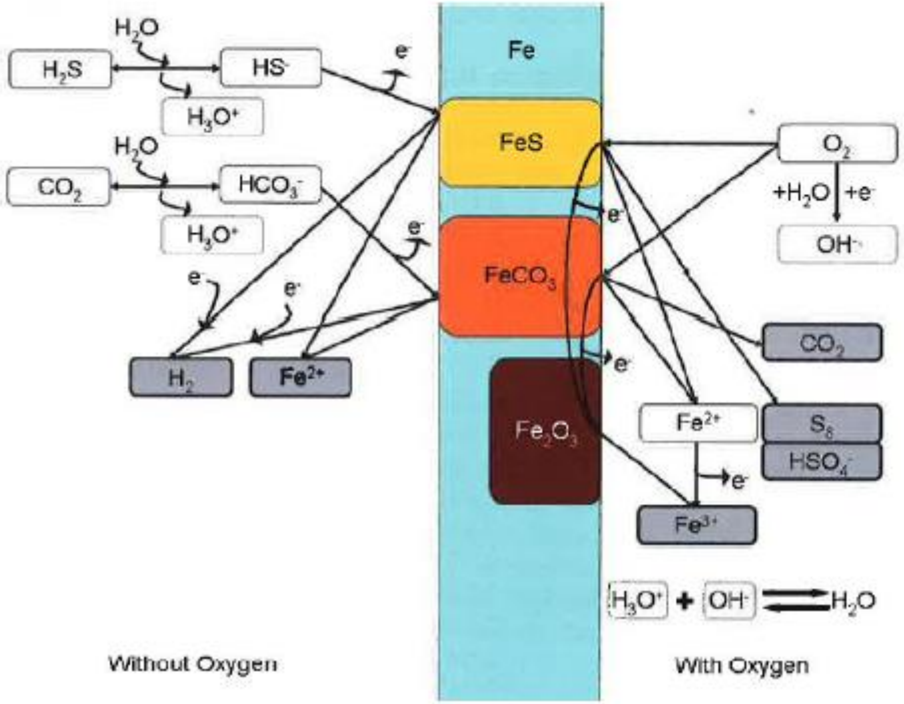
WP 3: Impact of oxygen

- **Literature survey on the impact of oxygen on geochemistry of underground gas storages**
  - No degradation mechanism linked to biomethane that has not already been identified in the case of natural gas
  - Greater amount of oxygen in biomethane composition could lead to the formation of higher amount of inorganic precipitates such as iron compounds
- **Principal conclusions**
  - The presence of biomethane contaminants could be a source of nutriments for subsurface micro-organisms (same as for natural gas)
  - Storage of biomethane underground may increase the risk of bacterial H_2S production by providing nutrients for existing bacterial communities
  - The potential species produced are for polythionate and possibly elemental sulfur
  - H_2S in underground gas storages can also increase acidity that can prematurely deteriorate the UGS

⇨ **Core flooding experiment using rock cores from representative reservoirs in order to evaluate the impact of biomethane contaminants on the risk of inorganic and biologically derived precipitates causing formation damages**

WP4: Impact of corrosive compounds

- Literature survey on oxygen and corrosive compounds on materials of gas infrastructures
  - Corrosion is influenced by several parameters
    - water,
    - flow,
    - water composition
    - gas composition such as the presence of CO_2, H_2S…
  - A higher corrosion rate is observed in presence of O_2 but this last does not increase linearly with oxygen contents. That can be explained by the formation of a passivation film
  - The presence of O_2 seems to induce more pronounced corrosion



The literature did not cover the real underground gas storage conditions, so we will conduct experiment with more representative concentration of O_2, H_2S and CO_2

Next phases of the project

Phase 2b and 2C programs proposals

- **WP1: Siloxanes impact**
  - Experimental program:
    - Industrial boilers: trials in reals operating conditions (start & stop)
    - Heavy duty vehicles: performances evaluation of the oxygen sensor in real conditions
  - Literature review:
    - Siloxane purification technologies
- **WP2: Sulphur impact on vehicle catalyst**
  - Experimental program:
    - Laboratory tests: catalyst behaviour with H_2S
    - Engine tests: sulphur impact on vehicle engine performances
    - Catalyst aging tests
    - Numerical modelling of catalyst behaviour with H_2S

The research program is based on the next 3 years and should be funded by 4.8 M€ from European Commission

Phase 2b: 2019 → 2021 (~ 1.8M €)
Phase 2c: 2020 → 2022 (~ 3M €)

Contributors of the next phases

(+ coordination)

Phase 2b and 2C programs

- **WP3: Oxygen and corrosives compounds impact**
  - Experimental program:
    - Biomethane formation damage mechanisms evaluation of underground gas storages
    - Microorganisms identification present in biomethane
    - Corrosion study on specific materials of gas infrastructures with oxygen and corrosive compounds from biomethane
    - Experimental study in order to evaluate the H_2 impact on storage tanks
  - Literature review:
    - Theoretical review of elementary sulphur formation mechanisms
    - Theoretical review of biomethane trace compounds impact on underground gas storages facilities
    - Literature review of H2 impact on natural gas
- **WP4: Improve biomethane knowledges**
  - Statistical study of biomethane composition data
    - Database on biogas and biomethane in the UK
    - Database on biogas and biomethane in Sweden
    - Correlation between substrates and purification technologies with biogas/biomethane composition and trace compounds
  - Trace compounds into bioGNL
  - Comparison of biogas treatment technologies

Conclusions

Conclusions

The previous work allowed to identify which gas infrastructure could be impacted by biomethane trace compounds

- **Siloxanes:**
  - After combustion: oxidation in silica
  - Deposition on cold parts of the
  - Ionization sensor
  - Oxygen sensor
  - Refractory material abrasion in industrial boiler
- **Sulphur:**
  - Metal and ceramic catalyst deactivation in presence of water
- **Oxygen and corrosive compounds in underground gas storages:**
  - No proper risks link to biomethane trace compounds
  - Higher concentration of H_2S, O_2 and CO_2 compare to natural gas can cause a premature damages on underground gas storages

Thanks for your attention

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