

Result of MARCOGAZ "WG Gas Quality & Biogas" benchmark on sulphur in natural gas

Context

Sulphur in gas come from two different origins:

- Sulphur present originally in gas;
- Sulphur coming from odorant.

To prevent impacts on infrastructures, end-users equipment and environment, maximum quantity of sulphur is specified. The sulphur content for natural gas may be expressed using three specifications:

- Total Sulphur;
- Mercaptans;
- H₂S.

During EASEE-gas preparation of the CBP Gas Quality the three expressions for sulphur content have been defined as follow:

- Total Sulphur < 30 mgS/m³ (n);
- Mercaptans < 6 mgS/m³ (n);
- H₂S and COS < 5 mgS/m³ (n).

These quantities are expressed in mg of Sulphur per cubic meter (mgS/m³ (n)).

The consensus on these values was achieved easily; however the specification addresses only gases without added odorant.

More recently some companies have expressed their interest in decreasing these sulphur specifications. MARCOGAZ "WG Gas Quality & Biogas" decided to have a view on the current situation on sulphur content in natural gas. This was done by enquiry circulated within MARCOGAZ Members.

Sulphur regulation in gas

In this section we detail the existing specification coming from national laws or Industry Guidelines that have to be enforced. Existing regulations on sulphur for natural gas are different for each Country. They are generally expressed using the above mentioned specifications.

The quantity of total sulphur ranges from 30 to 158 mgS/m³ (n); the quantity of mercaptan ranges from 6 to 17 mgS/m³ (n); the quantity of H₂S sulphur from 5 to 15 mgS/m³ (n).

Table 1: Sulphur regulation on gas by Countries

| | France | Austria | Belgium | Italy | Germany | Spain | United Kingdom | Netherlands | Czech Republic |
|---|--------|---------|---------|-------|---------|-------|----------------|-------------|----------------|
| Total Sulphur (mgS/m ³ (n)) | 150 | 10 | 150 | 158 | 30 | 50 | 50 | 45 | 30 |
| Mercaptan (mgS/m ³ (n)) | | 6 | | 15,8 | 6 | 17 | | 10 | 6 |
| H ₂ S (mgS/m ³ (n)) | 7 | 5 | 6,5 | 6,6 | 5 | 15 | 5 | 5 | 5 |

Note that in Germany, DIN 51624 "Natural gas for vehicle" is specifying a maximum sulphur content of 10 mg/kg or about 8 mgS/m³. This specification does apply only to gas as a vehicle fuel.

Technical specifications

Technical specifications are given by the main operators and are obviously complying with the regulation. For half Countries (Germany, Italy, Austria, Czech Republic, Spain) technical regulations on gas are similar to sulphur regulation on gas. For the others Countries technical regulations are more stringent than the regulation.

Table 2: Technical specifications by Countries

| Country | France | Austria | Belgium | Italy | Norway | Germany | Spain | United Kingdom | Netherlands | Czech Republic |
|---|--------|---------|---------|-------|--------|---------|-------|----------------|-------------|----------------|
| Total Sulphur (mgS/m ³ (n)) | 30 | 10 | 30 | 158 | 30 | 30 | 50 | 21* | 30 | 30 |
| Mercaptan (mgS/m ³ (n)) | 6 | 6 | 6 | 15,8 | 6 | 6 | 17 | | 6 | 6 |
| H ₂ S (mgS/m ³ (n)) | 5 | 5 | 5 | 6,6 | 5 | 5 | 15 | 5 | 5 | 5 |

*The original value is in ppm which was translated in mgS/m³ taking S as molecule.

Actual content before odorisation and addition by odorant

Actual content observed on the networks range from 1 to 30 mgS/m³. In Germany the average value is 4 mgS/m³ but the maximum can reach 18 mgS/m³ (only for max 2% of gas). A similar situation is observed in Italy.

Table 3: Actual content before odorisation and addition by odorant

| Country | France | Austria | Belgium | Italy average and (maximum) values | Norway | Germany average and (maximum) values | Spain | United Kingdom | Netherlands | Czech Republic |
|--|--------|---------|---------|------------------------------------|--------|--------------------------------------|-------|----------------|-------------|----------------|
| Total Sulphur (mgS/m ³ (n)) | 6 | 3 | 8 | 1,05 (80) | 30 | 4 –(18) | 6 | 6 | 5 | 3 |
| Mercaptan (mgS/m ³ (n)) | 2 | 3 | | 0,02 | 1 | 1 | 1 | | 5 | 1 |

| | | | | | | | | | | |
|---|-----|-----|-----|------|-----|-----|-----|-----|-----|-----|
| H ₂ S (mgS/m ³ (n)) | 5 | 1 | 6 | 0,03 | 5 | 1 | 1 | 4 | 5 | 2 |
| Total Sulphur added by THT (mgS/m ³ (n)) | 9,1 | 4,7 | 7,3 | 14,7 | 5,2 | 6,0 | 8,0 | / | 6,5 | 4,4 |
| Total Sulphur added by mercaptan odorant (mgS/m ³ (n)) | / | / | 2,2 | 3,8 | / | 0,6 | / | 2,5 | / | 3,9 |

Note: The sulphur addition from odorant expressed here is the average sulphur addition stated in the report from MARCOGAZ WG "Odourisation" (GI-OD-11-05).

For odorised gas, the quantity of sulphur increase due to sulphur coming from odorisation. The worse case is when the odorant used is THT.

Regulation on SO_x emissions

Sulphur content may also be driven by regulation on SO_x emission. Maximum SO_x emission are regulated in all EU countries, the regulation being expressed in terms of maximum SO_x concentration expressed in mgS/m³ of dry fumes brought back to a given content of Oxygen, typically 3, 5 and 15%.

These three expressions are corresponding to the typical air-gas ratio of respectively boilers, engines and turbines.

New European Industrial Emissions Directive (IED – 2010/75/UE) published in 2010 accepts maximum level for SO_x of 35 mgSO₂/m³(n) for gaseous fuel used in combustion facilities at 3% O₂.

Generally the regulation on SO_x emissions depends on the thermal power of the installation and may differ according to the power. In the table below the most stringent limits have been retained.

Table 4: Regulation on SO_x emissions

| Country | France | Belgium | Italy | Germany | Spain | United Kingdom | Czech Republic |
|--|--------|---------|-------|---------|-------|----------------|----------------|
| Boilers (3% O ₂) (mgS/m ³ (n)) | 15 | 35 | 35 | 10 | 35 | 10 | |
| Turbine (15% O ₂) (mgS/m ³ (n)) | 10 | 12 | | 12 | | 10 | |
| Engines (5% O ₂) (mgS/m ³ (n)) | 30 | | | 9 | | 50 | 35* |

*given at 6% of O₂.

According to these values, one can calculate the maximum amount of total sulphur in the gas leading to emission limits, considering that:

- All SO_x emissions are coming from the combustion of S present in the gas and lead to SO₂ (S+O₂→SO₂);
- 1 m³ of natural gas produces 9 m³ of dry fumes (V_f) under stoichiometric conditions.

$$m_S = \frac{M_S}{M_{SO_2}} \cdot \frac{m_{SO_2}}{1 - \%O_2 \text{ fumes} / \%O_2 \text{ air}} \cdot V_f$$

The molecular mass of S is 32g/mol and SO₂ is 64g/mol.

Percentage of oxygen in fumes is 3, 5 or 15% according to the type of installation taken into account.

Percentage of oxygen in air equals to 0,209.

The mass of SO₂ is given by the regulation.

Table 5: Maximum total sulphur in gas

| Country | France | Belgium | Italy | Germany | Spain | United Kingdom | Czech Republic |
|---|--------|---------|-------|---------|-------|----------------|----------------|
| Boilers (3% O ₂) (mgS/m ³ (n)) | 79 | 184 | 184 | 53 | 184 | 53 | |
| Turbine (15% O ₂) (mgS/m ³ (n)) | 159 | 191 | | 191 | | 159 | |
| Engines (5% O ₂) (mgS/m ³ (n)) | 177 | | | 53 | | 296 | 207 |

Thus, if all SO_x come from natural gas sulphur compounds, a maximum of 53 mgS/m³(n) for total sulphur species can be allowed in the gas to comply with the more stringent regulation in EU.

Conclusion

Except for the peculiar case of natural gas as a vehicle fuel in Germany where the maximum sulphur content is about 8 mg/m³(n) the more stringent specification in EU Countries for sulphur species are:

- Total Sulphur: 10 mg/m³(n);
- Mercaptans: 6 mg/m³(n);
- H₂S: 5 mg/m³(n).

The mercaptan sulphur and H₂S **regulation** are similar in all Europe. For total sulphur regulation goes from 10 (Austria) to about 150 mgS/m³(n) (France, Belgium and Italy) Except Italy and Spain, in all Countries **technical specifications** on total sulphur is around 20-30 mgS/m³, for mercaptans (6 mgS/m³(n)) and for H₂S (5 mgS/m³(n)).

The **actual content** of sulphur in gas is generally well below the above values for total sulphur and mercaptan sulphur before odorisation although some gases could locally present very high sulphur contents.

The **addition** of sulphur from **odorisation** depends highly on the odorant used. It is about 10-15 mgS/m³(n) when THT is used and only 0,6-4 mgS/m³(n) when mercaptans mixtures are used.

In any case these sulphur contents are largely below that required by even the most restrictive regulation on **sulphur oxides emissions**.