
EUROMOT POSITION

4 April 2012



Total Sulphur Levels in Natural Gas with Special Consideration of IC Engines

1. Background

The EEASE Gas draft composition specification has following sulphur related emissions:

- Total S maximum 30 mg/m³
- H₂S + COS (as S) maximum 5 mg/m³
- RSH (as S) maximum 6 mg/m³

The European IC Engine Industry – EUROMOT - has made following recommendation **11**:

- Total S maximum 5 mg/m³
- H₂S + COS (as S) maximum 5 mg/m³
- RSH (as S) maximum 0 mg/m³*

*Sulphur free odorants are preferred

Consequences if natural gas will contain the maximum sulphur compounds according to the EEASE GAS composition proposal are:

- Severe corrosion expected in the heat recovery system and stack of existing CHP (Combined Heat and Power) plants and new plants will have to use very expensive cold corrosion resistive materials in their design or operate at lower total efficiencies.
- Emission limits are continuously getting stricter and in order to comply catalysts are

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needed, but oxidation catalyst performance will be reduced or severely inhibited (dependent on gaseous component in focus) by the SO₂ in the flue gas. Possible non-compliance with current/future stipulated emission rulings will be the consequence.

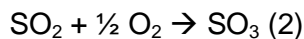
In below text more information about the expected big challenges with high concentrations of sulphur compounds in the natural gas can be found.

2. Enhanced Corrosion Risk

In the heat recovery system of a natural gas fired CHP plant, flue gas is often cooled to low temperatures: e.g. in district heating plants well below 100 degree C; in order to recover valuable heat energy as efficiently as possible. Cold end corrosion might occur on surfaces that have a lower temperature than the dew point of the flue gas they face. Condensation of sulphuric acid is the most common cause to cold end corrosion. The sulphur compounds in the fuel is oxidized to SO₂ (sulphur dioxide) in the engine cylinder:

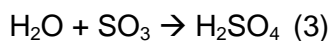


A fraction of the SO₂ is oxidized to SO₃ (sulphur trioxide):

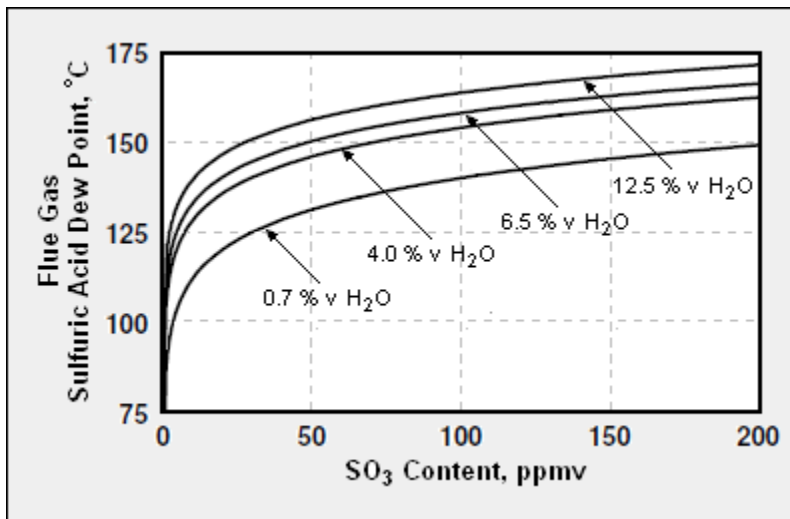


SO₃ concentration of the flue gas depends on many factors such as: SO₂ concentration, temperature, excess O₂, **presence of catalysts in the exhaust gas train**, etc.

SO₃ forms together with H₂O (water) sulphuric acid at temperatures at or below the dew point of the flue gas.

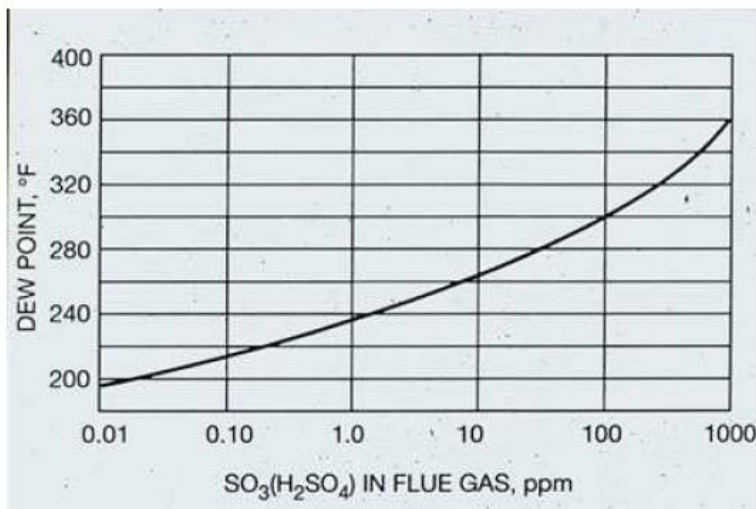


Due to the presence of gaseous sulphuric acid, the sulphuric acid dew point of the flue gas is much higher than the water dew point of the flue gases. Natural gas contains more hydrogen than fuel oils and thus combustion will result in a flue gas with a higher moisture content when burning gas. In below picture 1, the calculated sulphuric acid dew point of typical flue gases is given as function of the SO₃ and water vapour contents. It can be seen that a higher water vapour content of the flue gas raises the acid dew point temperature.



Picture 1: Calculated sulphuric acid dew point of the flue gas as function of SO₃ and water vapour contents /2/

Below picture 2 shows the dew point curve for a flue gas moisture content of 10 vol-%.



Picture 2: “Muller’ s” curve indicating acid dew point /3/

From above picture 2 can be seen that already small SO₃ contents of the flue gas will result in low dew point temperatures (e.g. 10 ppm-v < 130 degree C, 0.01 ppm-v < 93 degree C) of the flue gas.

A total S content of 30 mg/Nm³ (proposed EEASE gas max. limit); about 10 times higher than current typical German average value of 3 mg/m³; will lead to an increase of the SO₂ in the flue gas with about 2 .. 3 ppm-v. This increase “feels” low, but the impact might be big!

Sometimes up to 5 % [/2/](#) ...10 % [/3/](#) of the SO₂ might be oxidized to SO₃. As a consequence the dew point temperature will increase rapidly (see picture 2).

In practice it have been seen that a typical maximum S-content range of about 5 mg/m³ of the natural gas will not lead to excessive corrosion of the exhaust gas train components (boiler, exhaust gas ducting and stack). But in some installations with the natural gas sulphur contents of today, corrosion products (metals) have been found in the condense water due to the sulphuric acid corrosion, thus with the proposed EEASE gas composition big corrosion impacts can be expected at least in many existing CHP installations.

3. Future emission limits and catalyst needs

Emission limits are continuously getting stricter and new species are added to the regulated list. Currently in focus are emissions being considered detrimental to human health such as CO (carbon monoxide), formaldehyde and in some jurisdictions additionally ozone precursors i.e. VOC (volatile organic compound). VOC definition varies: in US VOC is NMNEHC (methane and ethane are excluded) and in EU VOC is defined as NMHC (methane excluded). In reference [/4/](#) is a list of the US VOC species can be found.

Stationary gas fired reciprocating internal combustion engines (RICE) have fast start up/shut down times, good part load efficiency and plant is compact. Stationary gas fired RICE are thus an “enabler” for intermittent sustainable power sources such as wind and solar power by efficiently supporting the grid stability of the electrical network when needed. This supports the EU 20-20-20 renewable energy target. The natural gas pipeline is in fact also a big storage of energy in energy disturbing cases. Local decentralized efficient gas fired CHP RICE plants are thus also enhancing the energy security in EU.

In oxidation catalysts noble metals are used and these are prone to deactivation/poisoning from the SO₂ content of the flue gas. With respect to the proposed new EEASE gas quality specifications the maximum sulphur content is a truly worrying aspect in terms of its impact on using catalyst technology especially for the future. It is expected that future more stringent requirements on emission requirements for even lower emissions, will necessitate a broader implementation of catalyst technologies. Below a short overview is given taking into account of some specific cases for lean-burn (LB) gas engines including gas fired dual fuel engines.

Regenerative/recuperative thermal oxidizers [/6/](#) are commercially available but these are not suitable for fast starting compact gas fired RICE. Natural gas, etc. might also be needed in

these oxidizers to maintain the high ignition temperature needed for the oxidation and thus decreasing the total efficiency of the power plant. The thermal oxidizers are very big in size, have a long start up (heating up time) and thus a compact oxidization catalyst suit the RICE plant better.

Today a common purpose for catalyst technology for LB gas fired engines is to remove carbon monoxide (CO) and formaldehyde. With reference to the proposed EEASE gas maximum sulphur concentration in the natural gas and the use of catalyst for such a purpose, there are currently available some oxidization catalyst applications sufficiently tolerable as per the proposed sulphur levels (but acceptance is anyway to be checked in beforehand with catalyst vendors, if OK or not). For some existing installations the EEASE gas specification might result in increased SO₂ oxidation to SO₃ and thus increased corrosion issues (see chapter above) or/and deactivation of current oxidation catalysts leading to higher emissions (non compliances with emission limits).

The big challenge will in particular be for VOC oxidization catalysts and especially if THC (Total HydroCarbons) including methane also will be regulated in the future. The shorter chain alkenes: methane, ethane and propane are stable molecules and difficult to oxidize (methane most difficult, next ethane and then propane). The proposed EEASE gas sulphur concentrations would in practice limit very much the possibility to apply certain type of catalysts commonly known to be fitted for oxidation of such critical components. This might prevent totally to reach the VOC limits already of today for new plants, prevent existing plants to fulfil their permit requirements due to deactivation of the currently installed catalysts.

In the future one can expect the need for sophisticated catalysts developed for removing THC including methane. This is a technology field under development at the moment and many challenges are still to be resolved (durability of the catalyst in the long term, regeneration philosophy, high ignition temperature need, etc.). There are strong indications that regeneration of such catalysts is needed already with the sulphur levels present in natural gas of today – the regeneration consumes energy and is quite challenging to be carried out in a controlled manner. Laboratory tests have shown that already 1 ppm SO_x concentration in the flue gas deactivates the CH₄ oxidation catalyst rapidly and also to some extent inhibits C₂H₄ and C₃H₈ reductions. This is due to the selective adsorption of SO_x on the very active PdO forming less active PdO-SO_x sites ^{15/}. Palladium (Pd) is needed in oxidation catalysts meant for high CH₄ oxidation, Platinum (Pt) is considerably less active for methane oxidation than Pd.

Along with the increase of sulphur content of the natural gas, the frequency of regeneration is

expected to grow dramatically and hence increase the use of natural gas or other energy source for the ignition of the application. This will unavoidably lead to unfeasible total operating cost of such a plant but can also mean in such high proposed sulphur contents that the methane oxidation catalyst becomes in practise useless.

Generally we believe that, if the natural gas quality becomes worse in terms of its sulphur content, it will have a dramatic impact on the BAT emission definitions and levels for lean-burn gas engines in the future compared to the scenario with currently available natural gas. This will have a contradictory impact on the emission reduction needs, and of course directly will increase emissions of sulphur oxides. Further the impacts on the existing e.g. VOC oxidation catalysts applications in the field should be understood and taken into account.

4. Recommendation

EUROMOT has in above text highlighted the consequences of high sulphur compounds content of the natural gas; an about 10 times higher level (3 to 30 mg/m³ increase) than typical today.

Many existing CHP installations will face severe cold corrosion and will have to operate at lower total efficiencies (increase flue gas temperature in stack with additional economical losses) if possible or invest in expensive corrosion resistive structures. New plant investment costs will increase due to need of better materials.

Some existing gas fired RICE might have to invest in new oxidization catalysts which are SO_x resistive in order to comply with todays emission limits. Future VOC and especially possible THC including methane emission limits require special catalysts based on Pd. Pd is very sensitive to SO_x and a high total S content and other sulphur components of the natural gas might inhibit usage of oxidization catalysts for emission compliance. Thermal oxidizers are too big, expensive and slow to be a realistic alternative especially in local decentralized CHP or grid stabilization stationary gas fired RICE plants.

EUROMOT has thus proposed a lower total S content of the natural gas, in line with levels of today and usage of a sulphur free odorant commercially available in order not to hamper the EU 20-20-20 and future emission targets.

One should also take into account the natural gas conditioning in a smaller scale at many sites is far more less economical than in the centralised units before the distribution into the pipeline.

5. Sources

- /1/ EUROMOT: [Gas Quality Aspects for Reciprocating Gas Engines](#), May 2011
- /2/ [Predicting Dew Points of Gases](#). Chemical Engineering Progress 78, F.H. Verhoff and J.T. Banchemo (1974)
- /3/ GE Power & Water: [Cold-End Deposition and Corrosion Control](#)
- /4/ US EPA: [Definition of Volatile Organic Compounds \(VOC\)](#)
- /5/ [Palladium catalyst performance for methane emissions abatement from lean burn natural gas vehicle](#); J. Lampert, M. Khazi, J. Farrauto, 1997
- /6/ [Regenerative/recuperative thermal oxidizers](#)

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Working Group Stationary Engines

EUROMOT is the European Association of Internal Combustion Engine Manufacturers. It is committed to promoting the central role of the IC engine in modern society, reflects the importance of advanced technologies to sustain economic growth without endangering the global environment and communicates the assets of IC engine power to regulators worldwide. For more than 20 years we have been supporting our members - the leading manufacturers of internal combustion engines in Europe, USA and Japan - by providing expertise and up-to-date information and by campaigning on their behalf for internationally aligned legislation. The EUROMOT member companies employ all over the world about 200,000 thoroughly skilled and highly motivated men and women. The European market turnover for the business represented exceeds 25 bn euros. Our **EU Transparency Register** identification number is **6284937371-73**.

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