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ADVANTAGE OF THE SUBSTITUTION ETHYLMERCAPTAN, COMPOUND FOR ODORIZATION NATURAL GAS, WITH TETRAHYDROTHIOPHEN

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Abstract:
This paper presents the advantage of substitution ethylmercaptan, compound for odorization natural gas, with other compound for odorization, tetrahydrothiophen. The physical - chemical properties of both compounds, ecological - toxic characteristics, odorization properties and evaluation of annual consumption odorization compounds in Serbia are discussed. The comparative analysis of these two odorization compounds from the aspect of chemical stability in the system of gas installations and economic acceptability have been described.

Keywords:
Ethylmercaptan, tetrahydrothiophen, odorization, substitution

1. INTRODUCTION

Natural gas, in particular, which is distributed for consumer goods, must be odorized up to level of one fifth of the lower flammable limit for security and health safety reasons.

Odorization compound with their physical - chemical properties should ensure first of all recognizable strong smell from a small portion of evaporation, or in a low concentration level to be detected leakage of gas and prevent unwanted consequences.

In Serbia as odorant, almost exclusively, used ethylmercaptan characterized with the best ability odorization, are no longer used in most European countries.

One of the main reasons for the termination of the use of ethylmercaptan as odorant its chemical instability (in the reaction with air and iron-oxide), which causes loss of smell intensity, as well as changes characteristic strong unpleasant smell.

Most frequently used compound for odorization natural gas is tetrahydrothiophen which has recognized intensive smell. It is the most stable of all gas odorants. Tetrahydrothiophen not react with iron oxides and bases and it does not change, nor the intensity or character of smell, for the most causes of loss of smell.

Unlike ethylmercaptan, which is extremely toxic to flora and fauna biosystem and the environment, tetrahydrothiophen belongs to the middle toxic group pollutant and there is no label danger for the environment according to the German classification for surface water pollutants. [4]

2. ETHYLMERCAPTAN (EM)

Physical - chemical characteristics:

- Chemical formula: C_2H_6S
- Appearance and the smell: colourless liquid – reminiscent of the smell of garlic
- Melting point: -148 °C
- Boiling point: 35 °C
- Density (g cm^{-3}): 0.839
- Flash point: -45 °C
- Explosion limits: 2.8 - 18.2 %
- Water solubility: slight

Other properties of ethylmercaptan:

- In normal circumstances, a stable, but extremely flammable liquid;
- Incompatible materials: oxidans (can lead to flammable), strong acid (reaction can be violent), calcium chloride (react violently), corrosive effect on metals, reacts violently with alkaline metals;
- Classification, belongs to the 3rd group of toxins and is extremely toxic to flora and fauna and surface water;
- UN number 2363;
- Additional tag 336; [5]

Ethylmercaptan as natural gas odorant

Ethylmercaptan has a very strong and unpleasant smell reminiscent of the smell of garlic. Threshold of low sensitivity of smell defined EM, based on its odorization capacity, as the best odorization compound for the natural gas. However, the big problem is nonstability of ethylmercaptan because it easily reacts with oxides and bases giving disulfide, and in that case loosing smell properties.

In addition, irreversible adsorption of ethylmercaptan on the walls of steel and polyethylene gas pipes increases ethylmercaptan consumption.

Low flammablity and extreme toxicity, associate with environmental and contamination aspect are the problems, because increase the cost of transport and storage. For these reasons ethylmercaptan as odorant need to replace with other substances with a higher chemical stability and less or slightly toxicity for the environment. [4]

Assessment of consumption ethylmercaptan in Serbia

According to company for natural gas odorization "OD – JU" from Ruma, the total amount of odorized gas in 2007. year was about 517,500,000 Sm^3. Total consumption of ethylmercaptan was about 6700kg, with the average achieved concentration about 12.95 mg/Sm^3 of natural gas. [3]

3. TETRAHYDROTHIOPHEN (THT)

Physical - chemical characteristics:

- Chemical formula: C_4H_8S
- Physical state and appearance: Liquid.
- Odor: strong unpleasant
- Molecular Weight: 120.11 g/mole
- Color: Clear Colorless.
- Boiling Point: 284.5°C
- Melting Point: 27.4°C
- Density: 1.26 (Water = 1)

Information about toxicity:

- Acute oral LD50 (in rats) 2450mg/kg
- Acute inhalation LC50 (in mice) 27g/Sm^3 (2 hours)

Environmental information:

Information about toxicity for aquatic organisms: No data available

Toxicity to Animals:

Acute oral toxicity (LD50): 1900 mg/kg [Mouse].

Acute dermal toxicity (LD50): >3800 mg/kg [Rat].

Tetrahydrothiophen as natural gas odorant

Tetrahydrothiophen has recognizable characteristic strong smell that is different from other spices impurities that may appear in the natural gas. THT shows very small deviations from own specific fragrance and is very difficult to overdose.

Tetrahydrothiophen is the most stable of all gas odorants, as a result of heterocyclic chemical structure, what is unusual for other common odorants. Tetrahydrothiophen not react with iron oxides and bases, and is imperceptible to most of the causes of pad smell.

Adsorption of tetrahydrothiophen on the walls of the new pipe is almost completely reversible so that the amount of THT is a reserve of odorant. In the case of changes in the dosage THT, dynamic equilibrium adsorption and desorption are disturbing and THT is desorbed from the wall of pipes back into the gas.

THT is in the middle group of pollutants according to the German classification of pollutants surface water (W6K2) and not wearing the label of danger for the environment, which makes it easier for packaging, storage and transport. [1, 4]

4. COMPARATIVE ANALYSIS OF ETHYLMERCAPTAN AND TETRAHYDROTHIOPHEN AS ODORANTS

Stability

The difference in stability ethylmercaptan and tetrahydrothiophen in the presence of corrosion on the walls of pipes is a significant benefit for the THT, which could be displayed in the chart (Figure 1).

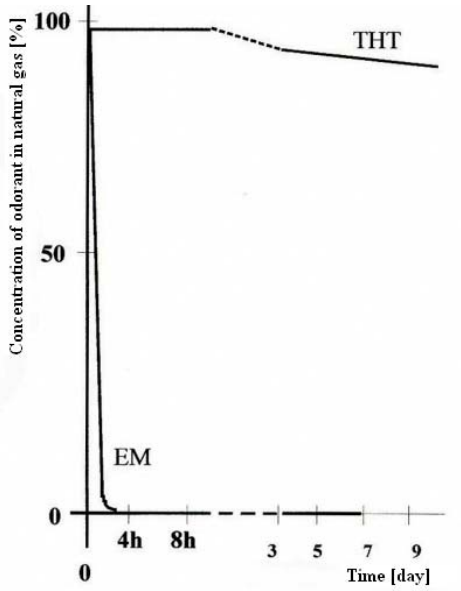

Figure 1. Graphic display depending on the concentration of odorant in function of time, in the natural gas in the presence of corrosion [4]

From the diagram it could be seen that the concentration of THT in the gas begins to decline significantly after the third day, while the concentration of EM decline in the "0" for about 2 hours. This means that the EM is totaly spent in the chemical reaction of oxidation, loosing completely smell in a very short time. [4]

Economic effects

Comparative analysis of the costs of the odorization with EM and THT in the following text is calculated for concentrations of odorant in the natural gas of 12.95 mg/Sm^3 for odorization 517.500.000Sm^3/yr, the average distance from odorants storage is about 80km.

Odorant ethylmercaptan

Total amount of required odorant is 517.500.000 Sm^3/yr • 0.00001295 kg/Sm^3 = 6700 kg/yr.
Price of charging for EM is 16.10 €/kg, (or 0.000241 €/Sm^3).
The annual price for EM is 16.10 €/kg • 6700 kg/god = 107,850 €/yr.

Odorant tetrahydrothiophen

Total amount of required odorant is 517.500.000 Sm^3/yr • 0.00001295 kg/Sm^3 = 6700 kg/yr.
Price of charging for THT is 31.02 €/kg, (or 0.000465 €/Sm^3).
The annual price for THT is 31.02 €/kg • 6700 kg/god = 207,850 €/yr. [3]

5. CONCLUSION

Replacement and substitution of ethylmercaptan by THT as the odorant for natural gas, is obviously required for the following reasons:

- For the protection of the environment bearing in mind its outstanding cumulative and biocumulativ toxic effect for flora, fauna, biosystem and environmental in general;
- Ethylmercaptan has unstable smell properties especially in the presence of oxide and base. This is particularly expressed in equipment and installations with compressed natural gas (LPG) for the cars;
- In Europe are generaly not used ethylmercaptan for odorization natural gas.
- The harmonization between national and international (EU) laws of regulations in the field of natural gas odorization with the EU.

According to real estimation, of the replacement procedure ethylmercaptan by tetrahydrothiophen can be completed in the next 3 to 4 years. [3, 4]

REFERENCES:

[1] DVGW Technischen Vorschriften G280-1/2004, G280/2004 und G2881
[2] Material safety data sheet tetrahydrothiophene msds, www.sciencelab.com/xmsds-tetrahydrothiophene
[3] OD-JU, konsolidovani finansijski izveštaj za poslovnu 2007. godinu, Ruma, 2007.
[4] Podolšak N., Milan Fistonić M., Usporedba svojstava komercijalnih kemijskih spojeva za odorizaciju plina – tetrahidrotiofena i etilmerkaptana, Stupnik, 2005.
[5] Safety (msds) data for ethylmercaptan, msds.chem.ox.ac.uk/et/ethyl_mercaptan.html