The olfactory of odourised biomethane: a novel approach

E.A. Polman, W.P. Brouwer, B.J. Gerritsen

Introduction

By now, biomethane is injected in the gas grid at about two hundred injection sites in Europe. The gas injected is odourised locally. Since some customers in practice may be supplied by 100% of biomethane, it is of utmost importance that the injected gas is recognized as natural gas.

Natural gas as well as biomethane are odourised for safety reasons.
The criteria for odourised gas in the Netherlands are, that the smell should be:

- alarming
- distinguishable
- not pleasant
- sufficiently strong to notice at 20% LFL

The control on a correct olfactory of natural gas is arranged in national regulations and is based on a control of the odourant level and of the olfactory. In most countries the olfactory of the gas is controlled by means of a panel. The strength of the smell as well as the nature of the smell is judged according to a well described procedure. For natural gas the olfactory is mostly sufficient when it is odourised properly, although in practice a disturbance of the smell, due to the presence of aromatic or sulphurous compounds, is possible.

Problem definition

With the introduction of biomethane, a whole new situation for the determination of the olfactory arose. For a substantial amount of samples, the typical smell of the odourant could not be recognized, even when these were odourised at the right concentration level. The nature of the smell was occasionally changed due to the presence of odoriferous compounds. The method used for odourised natural gas was no longer valid, since the strength of the smell was not enough basis to qualify the sample. This meant that a new method had to be developed, in order to qualify the olfactory of biomethane in a uniform way.

Odoriferous components in biomethane

Analysis of the samples show that in many cases, terpenes stemming from organic waste are able to disturb the olfactory. Also sulphurous compounds as hydrogen sulphide and mercaptanes may cause a disturbance of the odour.
The strength of the odour is listed for approximately four hundred components by Devos et al.[1]. The definition of the strength of an odour was defined by Laffort by means of the 'olfactory power' abbreviated by "p.ol (volume)"[2]. The olfactory power is a number, representing the negative log of the concentration expressed in volume or molar fractions for the threshold value for detecting a component by sniffing with the nose. In this way the strength of various components can be compared in a simple manner: the higher the number for the olfactory power, the stronger the smell. Devos et al. tried to make a set of consistent

data out of the results of many olfactory experiments from different laboratories. They did this by comparing the results, leaving out the inconsistent results and give weighting coefficients to data sets. These weighting coefficients are in fact correction factors. Some experimental results of the olfactory power have been corrected by two units or more. This means that results between different laboratories on the concentration where a smell can be detected, may vary with a factor of 100 or more. This shows that the results of Devos et al. give a good indication of the olfactory power of individual components in air, but that there is a large uncertainty in the quantitative interpretation.
The olfactory power for the mean value of some components, after applying weighting coefficients, is given in table 1.

Table 1: Olfactory power for some components according to Devos et al. [1]

Component	***Olfactory power (volume based)***
Tetra hydro thiophene (THT)	9.13
Hydrogen sulphide (H_2S)	7.75
Carbon disulphide (CS_2)	7.02
Limonene	6.36
Pinene	6.16
Toluene	5.81
Benzene	5.44
Butanone	5.11

THT, that is used in the Netherlands as odourant at a nominal level of 18 mg/m_n^3, has a strong odour, according to the findings of Devos et al.. According to the values in table 1, the smell of the terpenes limonene and pinene, is a factor 1000 lower as for THT.

Method for detection of the olfactory of natural gas

The method for detection of the strength of the odour as well as the nature of the smell for natural gas carried out at the laboratories of Kiwa is as follows:
A reference gas of THT in methane is mixed with an air stream in a Watson House odourimeter, resulting in a concentration of 0.10 mg THT/m_n^3 in air, representative for a concentration of 1% natural gas odorized at the minimum level in air, equivalent to 20% of the lower flammability limit (LFL). According to the Dutch standard NEN 7244-1, at 20 % LFL, the smell should be easily identified by the public as an alarming and unpleasant smell, and should also be associated with natural gas.
The reference smell is compared to the smell of a test sample in a glass bottle, that is mixed with air in a similar test rig. The air flow is 100 times larger than the test gas flow, resulting in a mixture of 1% gas in air.
Both samples are smelled and compared in a glass beaker by a qualified test panel of at least three persons. By adapting the air flow and gas flow, the strength of the test gas, related to the reference gas, can be determined.
For natural gas, the majority of test samples is qualified as sufficiently recognizable by its smell. Samples that are disqualified mostly have a THT concentration lower than the lower limit value of 10 mg/m_n^3 and can therefore be qualified as insufficiently odourised. A

sufficiently odourised natural gas sample with a smell deviating from the reference gas, is very rarely observed.

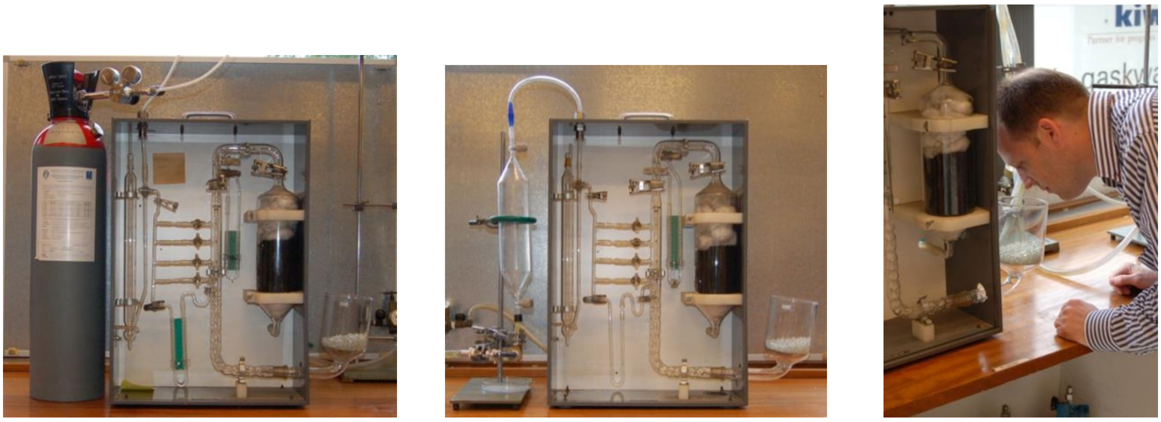

Figure 1, from left to right: reference gas odourimeter, sample gas odourimeter and detection of a gas mixture in a glass beaker

Urgency for a novel method

When measuring biomethane samples it turned out that for a substantial amount of test samples, the smell was deviating from the smell of THT. When the characteristic smell of THT can not be observed, this will directly lead to a safety risk, since a gas leakage can be associated to another phenomenon. Cagnon et al. have showed that a an unannounced change of the type of odourant leads to a significantly lower percentage of the public that associates the smell to natural gas (drop of 35% in the case of TBM and 65% for S-free ®) [3]. This clearly shows that it is of utmost importance that the smell of the gas is always associated to the smell of the odourant that people are used to. Any change of the nature of the smell will lead to a lower safety level.

The high numbers of deviating biomethane samples lead to an urgency to adapt the traditional method for the determination of the olfactory for natural gas, to a dedicated method for biomethane.

The novel test method was aimed to result in a standardized, transparent and objective procedure for the determination of the olfactory of biomethane.

The novel test method

A method was developed in order to evaluate a biomethane sample on the right criterion: is it likely that the biomethane injected will be recognized as natural gas? The method was discussed with Dutch grid owners and they concluded that this method was fit for the purpose. The procedure is outlined below.

A biomethane sample is taken on site and collected in four glass cylinders. The samples are transported to the laboratory and tested within 30 hours on olfactory by means of the Watson House odourimeter. A panel of at least three qualified persons smells the gas in a blind test and the members note their observations individually. They note the character of the smell and the strength of the smell.

In this method the smell can be classified into four main categories:

1. Gas smells like natural gas
   When the gas smell is identical to the smell of THT and the strength of the smell is sufficient, the sample is approved.

2. Gas smells like natural gas with a background odour of biogas
   The typical smell of THT is present but another smell can be observed as a background odour. When the strength of the smell is sufficient, the sample is approved. Upon request an additional chemical analysis can be made on trace components.

3. Gas smells like biogas with a background of natural gas
   A smell, not similar to natural gas, is dominating. However, the natural gas smell can still be observed as a background odour. It is not possible and useful to define the strength of the smell, related to the reference.
   In case of a gas leak, this gas may not be recognized by the public as natural gas. For this reason the biomethane sample gas is disapproved. Upon request an additional chemical analysis can be made on trace components.

4. Gas smells like biogas
   The sample has a smell not similar to natural gas and no natural gas smell can be identified at all. It is not possible and useful to define the strength of the smell, related to the reference.
   In case of a gas leak, it is likely that this gas will not be recognized by the public as natural gas. For this reason the biomethane sample gas is disapproved. Upon request an additional chemical analysis can be made on trace components.

This test method, dedicated for biomethane, is carried out about 200 times a year. A large number of data on the relation between the odour class and the components detected in the biomethane was obtained.

Results obtained for the new method

Typical smell characterizations from the panel are: sweet, butterscotch and sulphurous.
Analysis on various biomethane samples showed that the terpenes α-pinene, β-pinene, carene, cymene and limonene are occasionally found in biomethane. These components can be found in plants, particularly in pine trees, conifers and citrus fruits. These components all have a sweat and pleasant smell.
Also butanone having a butterscotch smell, is occasionally found in biomethane. Butanone may be an indication for incomplete digestion.
Furthermore the sulphurous components hydrogen sulphide, ethyl mercaptan, dimethyl sulphide and carbon disulphide were traced in some biomethane samples.
Since terpenes are regularly found in biomethane samples, a comparison between the amount of terpenes and the odour category was made. The concentration of terpenes is expressed as the total amount of terpenes and is outlined in figure 2. The biomethane is always odourised by the biomethane producer. Only samples with a proper THT level between 10 and 40 mg/ m_n^3 were selected for the dataset represented in figure 2.

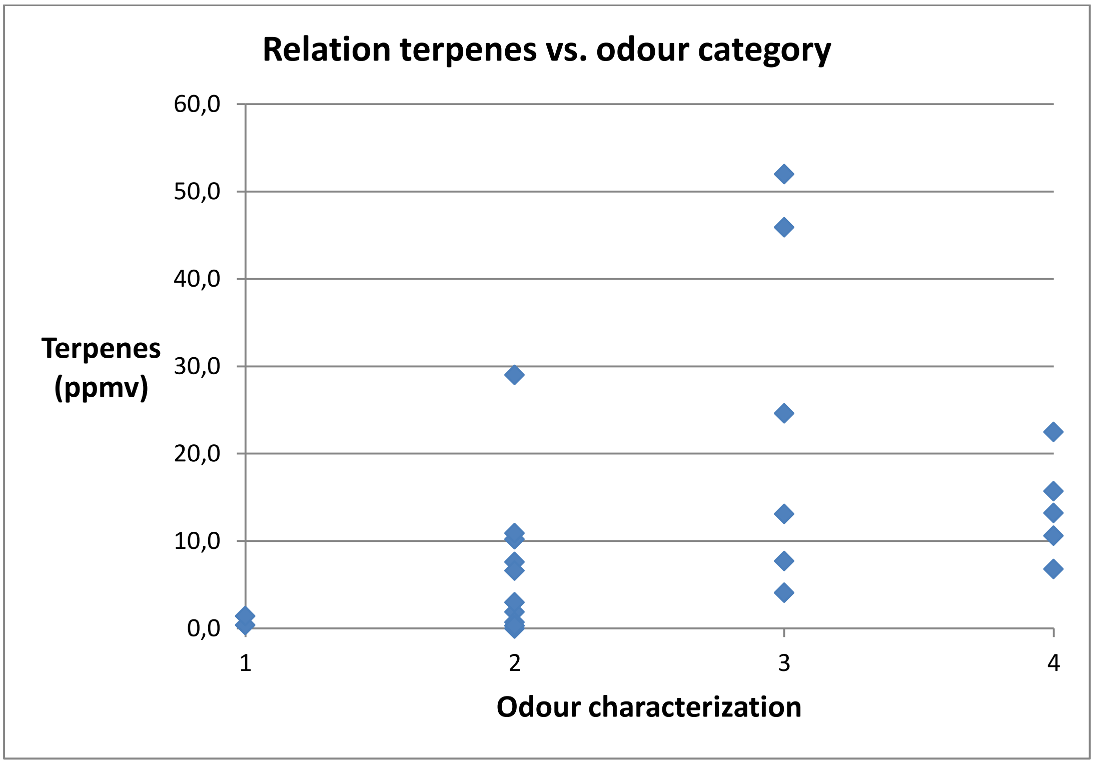

Figure 2: Total terpene concentration (ppmv) vs. odour category

Biomethane with a concentration below 1,5 ppmv of terpenes still smells like natural gas (odour type 1). Samples with odour characterization 3 and 4 show concentrations from 4 and 8 ppmv of terpenes respectively and higher.
The maximum concentration measured for terpenes was 52 ppmv.

Discussion

Although the olfactory panel shows a uniform assignment of the odour types, it is remarkable that biomethane samples with terpene concentrations of about 10 ppmv are assigned with odour category 2. This means that they can still be recognized as a smell similar to natural gas.
The total odour perception is an experience of many possible smells in a sample and can not simply be approached as an addition of individual odour strengths and odour characters. At first sight it seems remarkable that terpenes with an olfactory power thousand times weaker than THT, are able to suppress the THT smell at comparable concentration levels. Possibly the olfactory power is only a valid indicator for the smell strength at low concentrations and is not a good predictor for higher concentrations. It is also possible that the mixture of different smells leads to unpredictable and unexpected effects such as an increased strength of the smell.
Conditions that hamper a proper interpretation between the terpene concentration and the olfactory are the potential presence of other olfactory components such as sulphurous compounds that have not been analysed for all biomethane samples in the dataset. Furthermore the THT level in the analysed biomethane samples is not uniform and varies from 10 to 40 mg/ m_n^3. The THT concentration influences the strength of the natural gas smell.

Considering terpene formation, it is advised for biomethane producers to control their biomass input and biogas upgrading process, in order to achieve a terpene level not higher than 2 ppmv.

Conclusions

- A new method based on the assignment of odour types has been developed and successfully applied for the evaluation of the olfactory of biomethane samples.
- At low concentrations (4 ppmv and higher), terpenes are able to suppress the odour of the odourant THT.
- The relation between the terpene concentration and the odour type is not unambiguous.

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