Investigation of Methane-Hydrogen Mixtures in Vertical Pipelines

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Abstract

The paper presents an assessment of issues regarding the separation phenomena of methane-hydrogen mixtures in vertical pipelines. In the first part of the paper, the explosion risk is underlined. Thus, the widespread use of methane in both the industrial and domestic sectors is well known. In practice, due to recent trends, the injection of hydrogen into dedicated methane installations, the differences in densities can lead to separation phenomena which have an unfavorable effect on the operating regimes of equipment using this mixture and also, on the risk of explosion. The use of hydrogen in the industry is not new, but the increasing impact in terms of the number of users may involve a higher number of accidents due to the increased field of probability of hazardous situations in terms of explosions. The second part presents the used methods. The diffusion and gravitational separation are presented as phenomena having opposite effects. The used methods are theoretical and simulation approaches. The theoretical model is based on a nondynamic model. Therefore, no time parameter was not involved in the model. A linear dependence with the height of the concentration variation was observed for the range of heights considered. The conducted simulation underlined the same conclusion regarding the magnitude of gravitational separations in the methane-hydrogen mixtures. The main conclusion of the approach is that the separation phenomenon effect due to the gas density differences is negligible. The approach also revealed, as expected that the higher level of pipe is exposed to a higher risk of increased hydrogen concentration.

Keywords: investigation, methane, hydrogen, vertical pipelines, diffusion, gravitational separation

Introduction

Green technology prerequisites include hydrogen as a first option. Other options such as methane, propane, other crude oil derivatives, and coal are gradually coming off the scene.

Current technological maturity allows for the introduction of more environmentally friendly solutions, but economic competitiveness remains a challenge.

Therefore, hydrogen technologies are the preferred solution, but at the same time, the side effects they raise need to be anticipated. In this area, high-pressure storage solutions, stability of materials in contact with hydrogen, and, not least, explosion risks are issues that need to be addressed.

Until fully green solutions are adopted, the interest of nations is to move towards transitional solutions that will allow a gradual adoption without significant economic shocks. One such solution is the use of methane gas networks as a carrier for hydrogen produced from excess renewable energy.

At the European level, there have been significant developments in the conditions for the use of machinery in potentially explosive atmospheres offered by standards, both in terms of their number and the level of detail of technical requirements.

Hydrogen has been used in industry for a long time, but its use in domestic and transport applications is relatively new. Increased impact, in terms of the magnitude of the mass of users and the incidence of hazardous areas, may lead to an increase in the number of unwanted events, in terms of explosions.

In the approach to prevent new hazard situations, a good alternative is to start from a well-known current situation and then proceed by cautious extrapolation to the targeted area of much more frequent and widespread use of hydrogen.

Two European directives, known as ATEX, have been transposed into national legislation to implement explosion protection at the national level. Directive [**Chyba! Nenalezen zdroj odkazů.**] regulates the European market for products intended for use in

potentially explosive atmospheres but also the safe use of products. And Directive [**Chyba! Nenalezen zdroj odkazů.**] regulates the conduct of users of technical equipment and installations in the context of the risk of explosion.

All equipment intended for use in potentially explosive atmospheres must: be adequately protected against explosions [**Chyba! Nenalezen zdroj odkazů.**]; maintain the level of protection for the environmental conditions for which it was constructed; be able to withstand all foreseeable stresses to which it is subjected during storage, transport, installation, and operation.

Where Member States of the European Union adopt European standards which have been published in the Official Journal of the European Union and which include one or more of the essential health and safety requirements, equipment and installations complying with the applicable health and safety requirements are deemed to be accepted.

Risk of Explosion

The danger [**Chyba! Nenalezen zdroj odkazů.-Chyba! Nenalezen zdroj odkazů.**] and [**Chyba! Nenalezen zdroj odkazů.**] of explosion may accompany activities involving flammable substances. These may include raw materials, process intermediates, end products, and wastes from the usual production process. Since hazards from explosive atmospheres occur in a wide range of processes and operations, many branches of industry are affected by this risk. The explosion hazard lies at the intersection of three factors: the flammable substance, the oxygen, and the ignition source (Fig. 1).

Directives transposed into national law by [**Chyba! Nenalezen zdroj odkazů.**], [**Chyba! Nenalezen zdroj odkazů.**], [**Chyba! Nenalezen zdroj odkazů.**] and [**Chyba! Nenalezen zdroj odkazů.**] state that equipment and installations intended for use in potentially explosive atmospheres must have characteristics compatible with those of the explosive atmospheres [**Chyba! Nenalezen zdroj odkazů.**] in which they are to operate. Those directives define equipment groups and categories that classify the safety of equipment and installations according to their ability to maintain explosion protection under normal operating conditions, respectively under operating conditions in different fault scenarios.
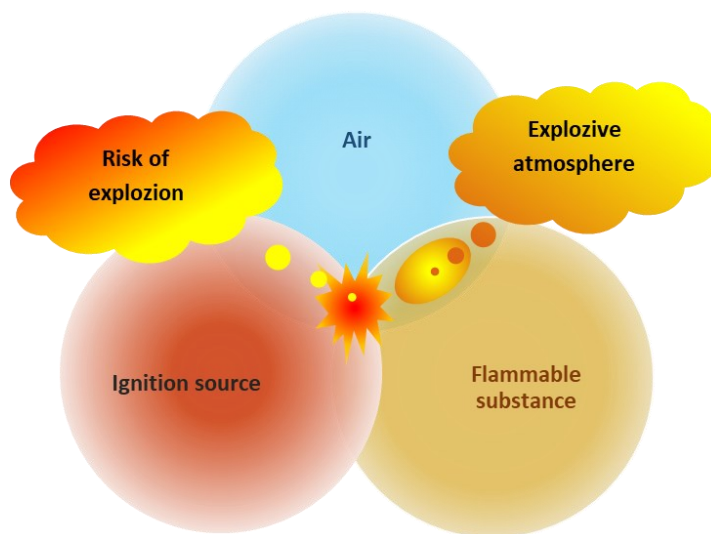

Fig. 1. Risk of explosion

To identify the influence on the risk of explosion induced by the use of hydrogen, a comparison of hydrogen with three other substances commonly used mainly for energy purposes (methane, propane, and butane) was carried out.

Fig. 1 shows a selection of the parameters presented in [**Chyba! Nenalezen zdroj odkazů.**] and [**Chyba! Nenalezen zdroj odkazů.**]: gas and vapor subgroup, self-ignition temperature together with temperature class, relative density to air, and flammability limits (concentrations).
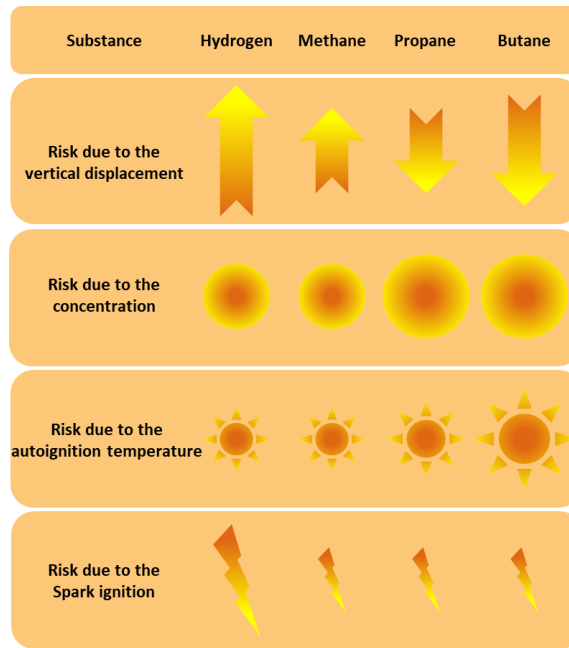
Fig. 2. Comparative risk diagram.

Diffusion and separation phenomena in methane-hydrogen mixtures

Hydrogen is expected to play a crucial role in reducing greenhouse gas emissions. Hydrogen is used in methane mixtures in dedicated methane distribution networks as an intermediate step.

Diffusion in gas mixtures is somewhat more complex than other phenomena such as thermal conductivity or viscosity. The difference in the average velocity of the two components (methane, hydrogen) leads to different diffusion velocities which cause a local pressure variation which in turn causes a mixture flow which in turn facilitates homogenization.

A difference in composition in a two-component gas mixture causes a relative flow of components that tends to become uniform. The flow of a component is proportional to the difference in concentration. Complementarily is balanced by an equal and opposite flow to the other component (Fig. 3).

The proportionality constant is the same for both components and is called the diffusion coefficient, for that pair of gases.

This relationship between flux and concentration gradient was formalized by Fick in his law of diffusion. The unit in the international system for the diffusion coefficient is a square meter per second (m^2/s). Diffusion is a slow process.
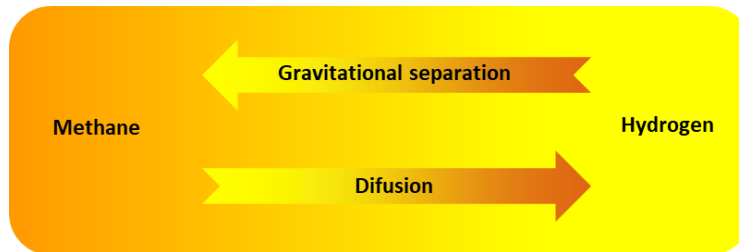

Fig. 3. Antagonistic processes in the methane-hydrogen mixture.

Gas diffusion coefficients at a pressure of one atmosphere and ordinary temperatures are mostly between 10^{-5} and 10^{-4} m^2/s.

Diffusion coefficients are inversely proportional to the total pressure or total molar density, but increase with increasing temperature but with pressure or total molar density held constant while the temperature is changed.

Considering the initial state of the methane-hydrogen mixture to be perfectly homogeneous with a predefined concentration of hydrogen in the mixture, one can define the final state of the hydrogen concentration distribution due to the effect of the gravitational field.

Without considering the dynamics of the mixture's gravitational separation phenomenon, the concentration distribution after reaching the equilibrium state is defined by equation (1).

The gradient of the pressure distribution of gas in the gravitational field has been considered according to equations (1) and equation (2) of the gases

$$\frac{dp}{dz} = -\rho g \qquad (1)$$

$$\rho = \frac{pM}{RT} \qquad (2)$$

where: g is the gravitational acceleration, ρ is the gas density; p is the gas pressure, T is the absolute gas temperature, R is the gas constant, z is the elevation and M is the molar mass of the gas.

This gives the differential equation (3)

$$\frac{dp}{dz} = -\frac{pMg}{RT} \qquad (3)$$

Which has the solution given by the equation (4)

$$\frac{p(h)}{p(0)} = \exp\left(-\frac{Mgh}{RT}\right) \qquad (4)$$

This is the ratio of the pressure at elevation h to the pressure at the base. In the following, this ratio will be noted as pr(h).

If the hydrogen-methane mixture is considered to consist of ideal gases then the calculated pressures become partial pressures and their ratio is equal to the ratio of the concentrations. This gives the equation (5)

$$k(h) = \frac{p_{rCH_4(h)}}{p_{rH_2(h)}} = \frac{1-c_{H_2}(h=0)}{c_{H_2}(h=0)} \exp\left(-\frac{(M_{CH_4}-M_{H_2})gh}{RT}\right) \qquad (5)$$

The relative variation of hydrogen concentration in the mixture is described by the equation (6)

$$\Delta c_{H_2}(h) = \frac{1}{1+k(h)} - c_{H_2}(h=0) \qquad (6)$$

Applying equation (6) for different concentrations of hydrogen in the mixture measured at the base (h=0), the diagram in Fig. 2 was obtained.

Fig. 4 presents the variation of hydrogen concentration in the mixture expressed in ppm as a function of elevation expressed in meters and initial baseline hydrogen concentration in the mixture.
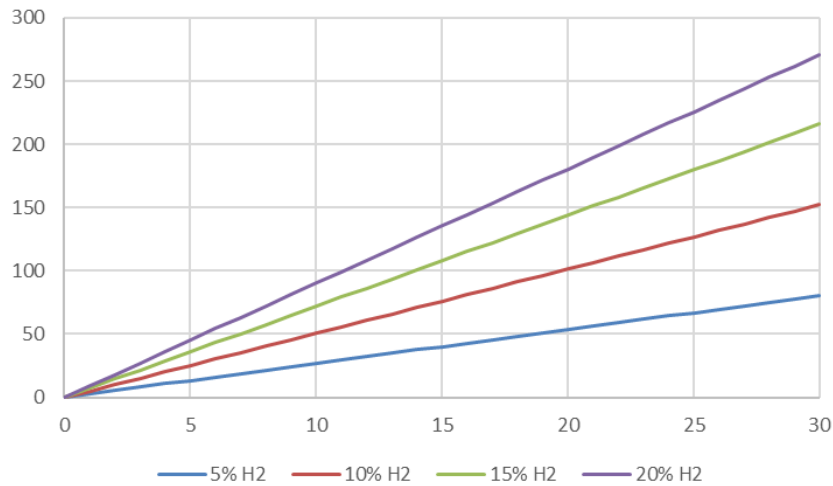

Fig. 4. Concentration variation due to gravitational effect.

The change in the hydrogen concentration of the mixture at a height of 30 meters at a base mixture with 20% v/v hydrogen concentration is about 271 ppm.

Similarly, with the base mixture concentration of 5% v/v hydrogen concentration, at the same elevation is about 80 ppm.

These variations of hydrogen concentration in the methane-hydrogen mixture do not induce problematic situations specific to high hydrogen concentrations for the analyzed height range.

The same phenomenon of gravitational separation was addressed by the simulation.

The following parameters were used to simulate the separation process of a methane-hydrogen mixture: a vertical pipe with an inner diameter: of 25 mm (1 in) and a length: of 29.525 m. For the length of the vertical pipe, 11 floors (10 + ground floor) with a height of 2.5 m each and 10 slabs with a thickness of 0.2 m each were considered. A further 0.025 m was added at the upper end to cover the section of the last horizontal pipe.

The first coupling (bottom to top) of the horizontal pipe is 2.5 m from the lower end of the vertical pipe. The other 10 horizontal pipes were coupled 2.7 m apart in height from the previous one.

For the horizontal pipes (11 pcs.) the inner diameter was chosen: 15 mm (1/2 inch) and the length: 2.5 m.

For the simulation process of gravitational effect in a vertical pipe filled with an initial homogeneous methane-hydrogen mixture was considered the physical parameters: system internal temperature: 293 K; pipe wall temperature: 293 K; internal pressure: 103325 Pa (20 mbar); gas composition: 10% v/v hydrogen, 89.1% v/v methane, 0.70281% v/v nitrogen, homogenized; pipe system was closed to avoid inrush/outflow currents; viscous pattern: laminar; time step: 120 s; the number of time steps: 3600 (5 x 24 h); measurement points for hydrogen and methane mole fractions: vertical and horizontal pipe junctions.
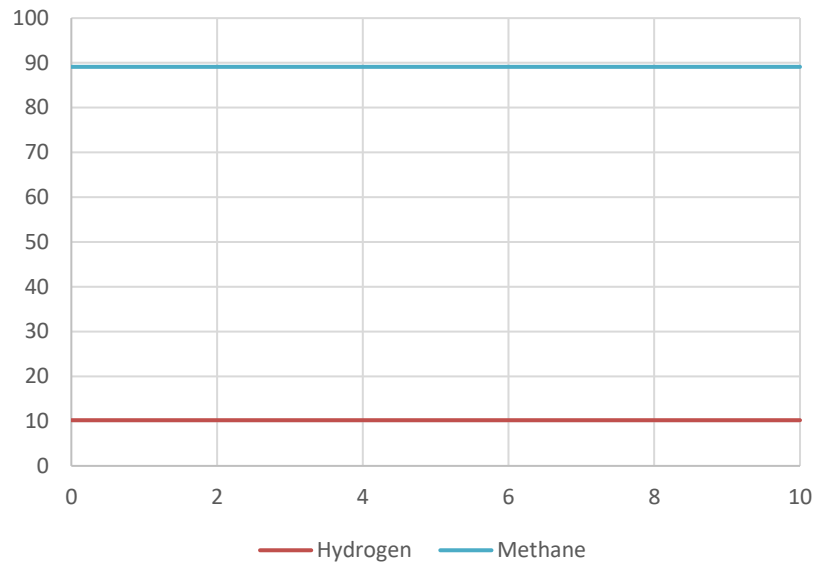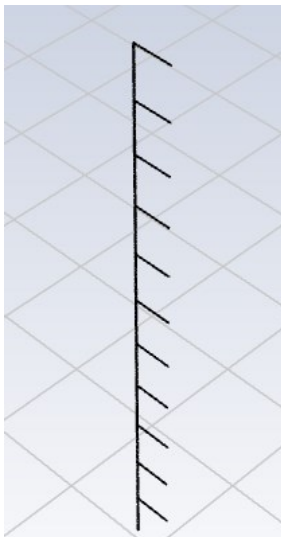
Fig. 5. Simulation of gravitational effect, configuration (left), and results (right).

In Fig. 5 (right) is observed that the concentration of the hydrogen does not visibly vary from analyzed point to point at the end of the simulation process.

Conclusions

Density differences between methane and hydrogen induce the gravitational separation phenomenon.

A linear dependence with the height of the hydrogen concentration variation was observed for the range of heights considered.

The change in the hydrogen concentration of the mixture at a height of 30 meters at a base mixture with 20% v/v hydrogen concentration is about 271 ppm.

Similarly, with the base mixture concentration of 5% v/v hydrogen concentration is about 80 ppm greater at the highest point.

The conducted simulation underlined not visible hydrogen concentration changes due to the gravitational separation phenomenon in the methane-hydrogen mixtures.

The approach also revealed, as expected that the higher level of pipe is exposed to a higher risk of increased hydrogen concentration.

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