

## Power-to-Gas: Safety Characteristics of Hydrogen/Natural-Gas Mixtures

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Safety characteristics for explosion protection of natural gas/hydrogen mixtures relevant in connection with the Power2Gas technology were studied in this work. Lower explosion limits (LEL) and upper explosion limits (UEL), limiting oxygen concentrations (LOC), maximum experimental safety gaps (MESG), maximum explosion pressures ( $p_{\max}$ ) and maximum rates of pressure rise  $(dp/dt)_{\max}$  were determined experimentally in dependence of the hydrogen fraction. Adding hydrogen did mainly effect the UEL, LOC, MESG and  $(dp/dt)_{\max}$ . The mixtures become more "critical" concerning the explosion hazards with increasing hydrogen fraction. However, the dependency of the safety characteristics from the hydrogen fraction is mainly not linear. Adding up to 10% hydrogen to natural gas had nearly no effect on the safety characteristics. More significant effects on the safety characteristics were observed at hydrogen fractions of more than 25%. For example the explosion group changes from IIA to IIB. Considering the huge explosion region and very high  $(dp/dt)_{\max}$  of hydrogen compared to natural gas, even adding 50% hydrogen to natural gas has a rather small effect on these characteristics. Furthermore  $p_{\max}$  of hydrogen/natural-gas mixtures can be calculated with good accuracy assuming ideal adiabatic conditions. EL and LOC of natural gas/hydrogen mixtures in ternary systems with inert gas and air were calculated in dependence of the type of inert gas with the so called "model of constant adiabatic flame temperature profiles" (Askar et al./2010).

### 1. Introduction

Power-to-Gas (P2G) is a simple method for the storage of excess energy that is produced by regenerative energy technologies like wind or solar power. Excess energy is used for the formation of hydrogen by electrolysis. Several P2G pilot-plants are already in use. For the storage of hydrogen the existing natural gas distribution grid and natural gas storages can be used. The consequences of the addition of hydrogen to the existing natural gas system has been studied extensively in several works regarding issues in different fields like chemical safety, material durability, efficiency, economy and environment. In the field of chemical safety substantial large scale tests like vapour cloud explosions in open space (Lowesmith et al./2011) and pipeline fires (Lowesmith et al./2012) have been conducted with methane/hydrogen mixtures within the project NaturalHy (Tiekstra/2008). The laminar burning velocity was studied by Huang et al./2006. The LEL and UEL of methane/hydrogen-mixtures were studied by Miao et al./2011 for example. Moreover some studies on the explosion pressure of methane/hydrogen mixtures have been conducted (Salzano et al./2012). Studies on the effect of inert gases on the explosion limits or on the LOC of such mixtures are hard to find (Zlochower and Green/2009). However, harmonized European standards for experimental determination of safety characteristics have mostly not been applied in previous works. Also there is a deficit on studies on other safety characteristics like MESG and  $(dp/dt)_{\max}$  and on mixtures with natural gas containing much longer-chain hydrocarbons.

In this work the effect of the addition of hydrogen to natural gas on explosion protection should be studied. For this purpose the existing data on safety characteristics for explosion protection from literature was evaluated and additional measurements were carried out. Pure methane as well as a natural gas with a high amount on longer-chain hydrocarbons was studied. Furthermore the applicability of methods for the calculation of safety

characteristics was tested. Considering the diversity of types of natural gas in practice and the different possible hydrogen fractions the high effort on experiments could be reduced significantly by using appropriate calculation methods.

## 2. Experimental methods

### 2.1 Test Gases and Mixture Preparation

Two types of natural gas were tested representing typical European natural gas compositions - one of dry type without longer-chain hydrocarbons (pure methane) similar to Russian or German natural gas and one of wet type with a significant amount on longer-chain hydrocarbons similar to northern sea natural gas (Altfeld/2012). Inert gases like nitrogen and carbon dioxide were neglected. In the following table the composition of the natural gas containing longer-chain hydrocarbons studied in this work is shown. Both gases were delivered directly by a gas supplier. The mixtures with different fractions of hydrogen, inert gas and air were prepared in a pressure resistant stainless steel vessel (autoclave) on site according to the partial pressure method. End pressure for the mixtures was 2 bar or 5 bar. It was assumed that the fraction of partial pressure corresponds to the mole fraction (ideal gas behavior). The mixtures were homogenized by a fan installed in the mixing autoclave for at least three minutes.

*Table 1: Composition of the wet natural gas studied in this work*

component	methane	ethane	propane	n-butane
mole fraction in mole%	89.3	8.0	2.0	0.7

### 2.2 Measuring equipment

For pressure measuring piezoresistive pressure transducers were used (company: Keller, type: PA10). For mixture preparation pressure transducers with a measuring range between 0 bar (abs) and 2 bar (abs) or between 0 bar (abs) and 5 bar (abs) were used. For measuring the explosion pressure, pressure transducers with a measuring range between 0 bar (abs) and 10 bar (abs) were used. The resolution of the pressure transducers is 10<sup>-4</sup> full scale full scale (FS). Resonance frequency is 30 kHz. Linearity is better than 0.5% FS. The pressure transducers have been calibrated by use of a high precision pressure measuring device. The ignition systems used are in accordance with EN 1839. The digitized signals of the measuring sensors are connected to an A/D-converter (company: Jet Systemtechnik GmbH, type: MCL-USB, 16 channels, 16 Bit A/D, sampling frequency: 500 kHz) and a computer for displaying, storing and evaluating the data.

### 2.3 Determination of explosion limits (EL) and limiting oxygen concentrations (LOC)

Determination of EL and LOC was carried out according to the European standards EN 1839 - tube method and EN 14756. Ignitions were carried out in a glass cylinder with a diameter of 80 mm and a length of 300 mm. Defined gas mixtures with air are introduced into the glass cylinder bottom up. The glass cylinder is purged with the mixture previous to all ignition attempts. Then an ignition is initiated in the quiescent mixtures with an electric spark (spark gap  $\approx$  5 mm, spark duration = 0.5 s) and it is observed whether or not a flame propagates through the reaction tube. Ignition criterion is a clear detachment of the flame from the electrodes and an upwards propagation over a distance of at least 100 mm. The highest and the lowest fuel gas concentrations, at which just no ignitions are observed, are defined as lower and upper explosion limits (LEL and UEL). The largest oxygen fraction in the ternary gas mixture with flammable gas, inert gas and air, at which the mixture is not explosive, irrespective of the amount of flammable gas being added is defined as the limiting oxygen concentration (LOC). For determination of LOC the concentration ratios of fuel gas, inert gas and air were varied systematically according to EN 14756. For determination of EL and LOC the non-ignitions were validated by at least four repetition tests respectively.

### 2.4 Determination of maximum experimental safety gaps (MESG)

MESG was determined according to EN 60079-20-1. The test apparatus consists of an inner volume and an outer volume, which are connected by a gap with a length of 25 mm and an adjustable diameter. The apparatus is made of stainless steel. The inner volume is equipped with an ignition source (spark ignition). In each test the test apparatus is purged with defined gas mixtures with air. Then it is ignited in the inner volume. Through a window it is observed whether the flame propagates in the outer volume. By varying the gap diameter and the fuel gas concentration in air systematically the highest gap width is observed at which just no

flame propagation from the inner volume in the outer volume is observed. The MESG is validated by at least four repetition tests.

## 2.5 Determination of explosion pressures ( $p_{\max}$ ) and rates of explosion pressure rise ( $(dp/dt)_{\max}$ )

$P_{\max}$  and  $(dp/dt)_{\max}$  were determined in accordance with EN 15967. Defined mixtures of fuel gas and air are ignited in a closed pressure resistant ignition autoclave of stainless steel with an inner volume of 14 dm<sup>3</sup> in quiescent condition using an exploding wire igniter (nickeline wire, diameter: 0.12 mm, distance of electrodes: 5 mm, ignition energy: 15 J). Simultaneously data acquisition is triggered. Measuring frequency is 20,000 Hz. The peak pressure and the maximum slope in the acquired pressure time curve is determined by the data acquisition and analysis software. The peak pressure for each curve is determined as the maximum moving average of ten values. The maximum slope of each curve is determined as the maximum slope of all regression lines. The number of values used for the regression lines is adjusted according to EN 15967 for each experiment, so that it is within a range (plateau A in Fig. 4), within which the dependence of the maximum slope on the number of values used for regression is preferably low. By varying the fuel gas concentration in air systematically according to EN 15967 the highest explosion pressure and the highest rate of explosion pressure rise in a closed system are determined for a certain fuel gas independent of the air fraction.  $p_{\max}$  and  $(dp/dt)_{\max}$  are validated by at least two repetition tests.

## 3. Calculation methods

Thermodynamic equilibrium calculations were carried out with the software "GasEq" (Morley/2005) available for free. The equilibrium temperature, equilibrium pressure and composition are calculated at constant pressure or constant volume by the minimization of the Gibbs free enthalpy assuming adiabatic conditions. The kinetics of the reactions is not considered. The following species were considered as product components:

C, CH<sub>4</sub>, CO, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, CH<sub>3</sub>, CH<sub>2</sub>O, H, H<sub>2</sub>, OH, O, O<sub>2</sub>, CH<sub>3</sub>CHO, HCO, CH, CH<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O, N<sub>2</sub>, CN, NH<sub>3</sub>, NO, NH<sub>2</sub>, NH, N, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, Ar

The explosion limits and limiting oxygen concentrations were calculated according to the semi-empirical model of constant adiabatic flame temperature profiles assuming a threshold flame temperature that must be exceeded as a criterion for flame propagation (Askar/2010). It is assumed that the profile of the threshold flame temperatures along the explosion regions boundary curve is constant for different types of inert gas and different initial conditions. Based on this assumption explosion limits are calculated in following steps.

1. Experimental determination of several explosion limits along the explosion region boundary curve in dependence of the inert gas concentration for a certain ternary system consisting of the components fuel gas, oxidizer and inert gas.
2. Calculation of the single adiabatic flame temperatures along the experimentally determined explosion region boundary curve in dependence of the inert gas concentration for this system.
3. Calculation of the explosion limits for another system with any type of inert gas and initial conditions by finding fuel gas concentrations with the same calculated adiabatic flame temperatures corresponding to the previously determined temperature profile in dependence of the inert gas concentration.

The flame temperature is calculated for adiabatic conditions without heat losses and at constant pressure assuming that the process occurs in the open. Consequently the influence of the apparatus is not considered. The calculation of the explosion limits was automated by means of a Microsoft Excel® macro linked to GasEq for the calculation of the flame temperatures.

## 4. Experimental Results

### 4.1 Explosion regions of natural gas/hydrogen mixtures

In Figure 1 the explosion regions of natural gas with different fractions of hydrogen are shown in a ternary diagram exemplarily. In table 2 explosion limits of methane and natural gas are shown in dependence of the hydrogen fraction added. The influence of the addition of hydrogen is very similar in both cases. The explosion region of pure hydrogen is much larger than the explosion region of pure natural gas. As would be expected by adding hydrogen to natural gas the explosion regions become larger. There is nearly no effect on the lower explosion limits (LEL), since the LEL of natural gas and hydrogen are nearly similar. But there is a significant effect on the upper explosion limits (UEL) and the limiting oxygen concentration (LOC). However the UEL as

well as the LOC do not increase linear with increasing hydrogen fraction. With 10% hydrogen the UEL and the LOC increase only very slightly. Even with 50% hydrogen the UEL is only increased by 75% compared with pure natural gas, whereas the UEL of pure hydrogen is more than 450% higher than the UEL of pure natural gas. The effect on the LOC is similar.

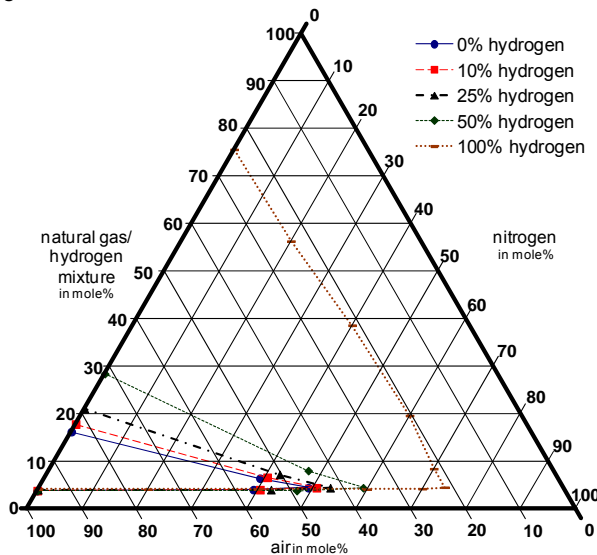


Figure 1: Explosion regions of natural gas/hydrogen mixtures with different hydrogen concentrations determined in this work (values for pure hydrogen taken from Molnarne et al./2008)

Table 2: Explosion limits of methane/hydrogen and natural gas/hydrogen mixtures determined in this work

hydrogen fraction in fuel gas blend	Methane/hydrogen			natural gas/hydrogen		
	LEL	UEL	LOC	LEL	UEL	LOC
0 mole%	4.2	16.6	10.1	3.8	16.2	9.7
5 mole%	4.2	17.4	9.8	3.8	17.2	9.7
10 mole%	4.2	18.2	9.6	3.8	17.8	9.4
25 mole%	4.2	21.2	9.1	4.0	21.0	8.9
50 mole%	4.0	29.0	7.9	3.8	28.4	7.6
100 mole%	4.1	75.6	4.3	4.1	75.6	4.3

#### 4.2 MESH of natural gas/hydrogen mixtures

MESH for methane/hydrogen mixtures (corresponding to dry natural gas) were determined by Physikalisch Technische Bundesanstalt (PTB, Braunschweig) (CHEMSAFE/2014). For wet natural gas MESH will still be studied at BAM. Similarly to the explosion regions, the MESH of methane and pure hydrogen are very different. Pure methane as the main component of natural gas has a MESH of 1.14 mm and is therefore allocated to the less critical explosion group IIA, whereas pure hydrogen is allocated to the most critical explosion group IIC with a MESH of 0.29 mm. In table 2 the MESH of mixtures of methane and hydrogen are shown. Similarly to the explosion regions with 10% hydrogen the MESH decreases only very slightly. However the dependency is more linear for higher hydrogen fractions. If more than 25% hydrogen is added the MESH falls below 0.9 mm and thus the mixture falls into explosion group IIB. At hydrogen fractions of more than 75% the mixture is allocated to explosion group IIC. Assuming a correlation of the MESH and the minimum ignition energy (MIE), a similar dependency of the MIE from the hydrogen fraction can be expected.

Table 3: MESH of methane/hydrogen mixtures (CHEMSAFE/2014)

hydrogen fraction in mole%	0	10	25	50	75	90	100
MESH in mm	1.14	1.10	0.96	0.75	0.52	0.33	0.29

#### 4.3 $p_{\max}$ and $(dp/dt)_{\max}$ of natural gas/hydrogen mixtures

With regard to  $p_{\max}$  the explosion severity of pure methane and pure hydrogen are very similar. But considering the  $(dp/dt)_{\max}$  hydrogen explosions are much more violent than methane explosions.  $(dp/dt)_{\max}$  of

hydrogen is about ten times higher than  $(dp/dt)_{max}$  of hydrocarbons. In Table 4 the explosion severity parameters of mixtures of methane and hydrogen are shown. Instead of the  $(dp/dt)_{max}$  the  $K_G$ -value is shown for better comparability. The  $K_G$ -value is the normalized  $(dp/dt)_{max}$ . It is calculated by multiplying the cubic root of the volume of the test apparatus assuming a nearly spherical vessel. As was observed for the other safety characteristics, it appears that adding 10% hydrogen to natural gas has negligible effects on the explosion severity parameters  $p_{max}$  and  $K_G$ . Even adding 50% hydrogen has a rather small effect on the  $K_G$ -value of natural gas considering the huge difference between the  $K_G$ -values of hydrogen and natural gas.  $p_{max}$  of the methane/hydrogen mixtures are very similar independent of the hydrogen fraction, due to the very similar  $p_{max}$  of hydrogen and methane.  $p_{max}$  and  $(dp/dt)_{max}$  of mixtures with wet natural gas will still be studied at BAM.

Table 4: Explosion severity parameters determined for methane/hydrogen mixtures in this work (values for pure hydrogen taken from Holtappels/2002)

hydrogen fraction in mole%	0	5	10	25	50	100
$p_{max}$ in bar	8.2	8.2	8.2	8.1	8.0	8.0
$K_G$ -value in bar*m/s	69	68	71	81	106	980

## 5. Calculation results

In Table 5 the results of the thermodynamic calculations of  $p_{max}$  and the experimental results are compared. The calculations are conservative, because of the assumption of ideal (adiabatic) conditions. The calculated  $p_{max}$  are constantly 0.8 bar higher than the experimentally determined  $p_{max}$ . The fuel gas concentrations in air, at which the explosion pressures are highest, correspond very well.

Table 5: Comparison of experimentally determined and calculated  $p_{max}$

hydrogen fraction	$p_{max}$ in bar		fuel gas fraction at $p_{max}$	
	experiments	calculations	experiments	calculations
0 mole%	8.2	9.0	10.5	10.0
5 mole%	8.2	9.0	10.8	10.4
10 mole%	8.2	9.0	11.2	11.0
25 mole%	8.1	8.9	12.6	12.2
50 mole%	8.0	8.8	16.0	16.6

Using the experimental data for the systems with nitrogen as inert gas for determining reference temperature profiles, the explosion limits and LOC of methane/hydrogen mixtures in systems with carbon dioxide as inert gas were calculated. Such mixtures are relevant in biogas plants for example. The results of the calculations are shown in comparison to experimental results in Figure 2.

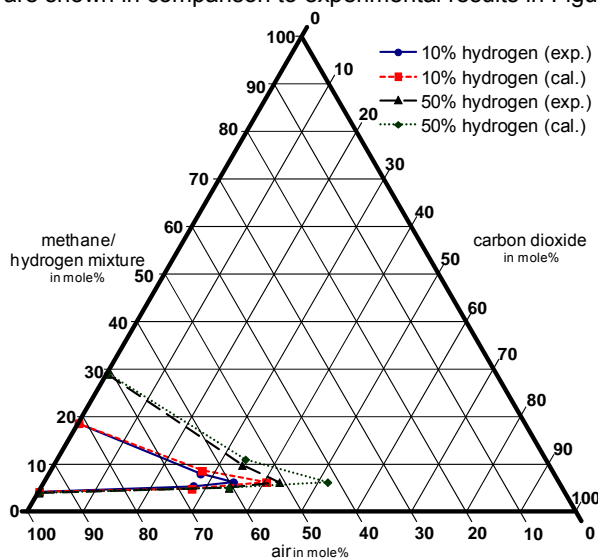


Figure 2: Calculated and experimentally determined explosion regions of methane/hydrogen mixtures in a ternary system with carbon dioxide and air

The deviation between the calculations and the experiments are highest at the apex of the explosion region. For the LEL and UEL near the apex the average deviation was 0.6 mole% (maximum 1.2 mole%). The average deviation at the apex was 7.4 mole% regarding the air concentration. Regarding the oxygen concentration the average deviation is 1.6 mole%. However evaluating the accuracy of the calculation method, the poorer experimental reproducibility of the apex compared to the other explosion limits has to be taken into account.

## 6. Conclusions

Adding up to 10% hydrogen to natural gas has nearly no effect on safety characteristics for explosion protection. Taking into account that the UEL, LOC, MESG and  $K_G$ -value of hydrogen are much more "critical" compared to natural gas, even adding 50% hydrogen to natural gas has only slight effects on these safety characteristics. The dependency from the hydrogen fraction is obviously not linear. Concerning the measures for explosion protection, adding hydrogen to natural gas in facilities designed for natural gas is technically possible without major modifications at least for hydrogen fractions up to 25 mole%. This applies to typical types of natural gas with higher amounts of longer-chain hydrocarbons as well as to pure methane. The results of the lab-scale tests in this work correspond very well with results of other works, where similar conclusions were drawn from open space tests (Tiekstra/2008). By means of thermodynamic calculations safety characteristics of mixtures of natural gas with hydrogen can be estimated with good accuracy. Experimental work could be reduced by means of such calculations.

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