

# Experimental Research of Flammability and Explosion Parameters of Binary Gas Mixtures in 1 m<sup>3</sup>

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This paper describes validation of a model for predicting the flammability and explosion of binary premixed mixtures of flammable solvents and gas vapours. To confirm the predictive efficiency of the derived parameters, the model was verified by comparing the predicted values with the experimental data for the studied premixed CH<sub>4</sub>/H<sub>2</sub>/O<sub>2</sub>/N<sub>2</sub> mixtures.

## 1. Introduction

Fuel-air mixtures are formed in plants, motors, combustion chambers and are subject to exothermal chemical reactions between fuel and oxygen, running in various explosive regimes: deflagrations or detonations. The evaluation of hazards associated to explosion of such mixtures is an important component of research in this field, based on determination of safety characteristic parameters in various conditions (Brandes and Möller, 2003). For deflagrations propagating in closed vessels, the most important safety parameters are the peak (maximum) explosion pressure, the explosion time and the maximum rate of pressure rise (Di Sarli and Di Benedetto, 2013). The explosion pressures and explosion times are important also for design of safety devices (vents), able to ensure active protection of pressure vessels where flammable mixtures are formed (Razus and Krause, 2001). In basic research, the peak explosion pressures are used for validation of propagation wave models and for calculation of the laminar burning velocity in various conditions (Razus et al., 2000, 2006). The present paper reports explosion pressures and explosion times of stoichiometric mixtures of lower alkanes (methane, ethane and propane) with air, calculated for various initial temperatures from 25 to 250 °C in heated 1 m<sup>3</sup> closed spherical vessel. The calculated peak explosion pressures of fuel-air mixtures are examined in comparison with the calculated adiabatic explosion pressures, obtained by means of dedicated computing program GASEQ.

## 2. Interest

The maximum explosion pressure is the highest explosion pressure over the flammable range in a closed volume at a given fuel concentration. Industrial interest: Fuel-air mixtures are formed in plants, motors, combustion chambers and are subject to exothermal chemical reactions between fuel and oxygen, running in various deflagrations regimes. The explosion pressures data are needed for design of safety devices (vents), able to ensure active protection of pressure vessels where flammable mixtures are formed. Gas explosion safety interest: Limited number of theoretical and experimental studies showing big maximum explosion pressure differences between the 120 dm<sup>3</sup>, 20 dm<sup>3</sup>, and 12 dm<sup>3</sup> at standard conditions. There are not reported theoretical and experimental studies of CH<sub>4</sub>/H<sub>2</sub>/O<sub>2</sub>/N<sub>2</sub> for 1 m<sup>3</sup> at elevated conditions. In basic research, the peak explosion pressures are used for validation of propagation wave models and for calculation of the laminar burning velocity in various conditions. The aim is to improve previous set of maximum explosion pressure calculations and extent it for the 20 °C - 250 °C initial temperatures and compare our theoretical and experimental results for ambient conditions.

### 3. Previous studies

Hydrogen-air is together with methane-air the most widely used mixture to demonstrate the validity of any new theoretical or experimental approach to determine its combustion or explosion parameters due to availability of many theoretical and experimental results using various techniques (Movileanu et al., 2011). Pekalski et al. (2005) used several thermodynamic models for explosion pressures calculation and compared with experimental data. To ensure the compatibility of data we selected the results for experiments that are in agreement with EN 13673-1 with the only exception that is volume of the testing vessel. (Holtappels et al., 2002) reports measurement of explosion pressures of hydrogen-air mixtures, at various initial concentrations close to stoichiometric (9.5 - 10.5 vol.%), in closed vessels of different volumes. The results have shown a similar behavior of investigated system. The maximum explosion pressures are  $(7.9 \pm 0.3)$  bar(a) for measurements made in the standard  $20.0 \times 10^{-3} \text{ m}^3$  spherical vessel. Higher deviations from these values are observed, however, when using smaller or larger size vessels, where radiative and convective heat losses to the walls could be neglected. (Cashdollar et al., 2000) reports different value of maximum explosion pressures for hydrogen-air mixtures, depending on the volume of the explosion vessel: 8.1 bar(a) in a  $120.0 \times 10^{-3} \text{ m}^3$  explosion vessel. The reported results from  $6.0 \times 10^{-3}$  are identical to those results obtained in the  $20.0 \times 10^{-3} \text{ m}^3$  and  $120.0 \times 10^{-3} \text{ m}^3$  despite the great difference in volume. (Razus et al., 2006) reports measurement of explosion pressures of methane-air mixtures, at various initial concentrations close to stoichiometric (9.5 - 10.5 vol.%), in closed vessels of different volumes. The results have shown a similar behavior of investigated system. The maximum explosion pressures are  $(8.3 \pm 0.3)$  bar(a) for measurements made in the standard  $20.0 \times 10^{-3} \text{ m}^3$  spherical vessel. Higher deviations from these values are observed, however, when using smaller or larger size vessels, where radiative and convective heat losses to the walls could be neglected. (Cashdollar et al., 2000) reports different values of maximum explosion pressures for methane-air mixtures, depending on the volume of the explosion vessel: 8.30 bar(a) in a  $20.0 \times 10^{-3} \text{ m}^3$  explosion vessel and 8.5 bar(a) in a  $120.0 \times 10^{-3} \text{ m}^3$  explosion vessel. The reported results from  $5.0 \times 10^{-3}$  are identical to those results obtained in the  $20.0 \times 10^{-3} \text{ m}^3$  and  $120.0 \times 10^{-3} \text{ m}^3$  despite the great difference in volume. The selected reference data are summarized in Table 1 together with the reported results from the 12-L sphere – see (Kondo et al., 2006) on dilution effect and (Kondo et al., 2008) on flammability limits. The reported results from the 12-L glass sphere are essentially identical to the results obtained in the 120-L sphere despite the great difference in volume and propagation criterion.

*Table 1: Measured and calculated explosion pressures of stoichiometric fuel-air mixtures at  $p_0 = 1 \text{ bar}$  and  $T_0 = 298 \text{ K}$ .*

| Fuel   | Stoichiometric equation   | Calculated (ECHIMAD) <sup>b</sup> | $p_{\max}$ (bara)<br>Calculated (COSILAB) <sup>b</sup> | Experiment (SPHERE) <sup>a</sup> |
|--|---|-----------------------------------|--|----------------------------------|
| Hydrogen (H <sub>2</sub> )<br>29.59 vol.%<br>$T_0 = 298.15 \text{ K}$<br>$p_0 = 1 \text{ atm}$ | $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$                | 7.99                              | 7.91   | 8.10                             |
| Methane (CH <sub>4</sub> )<br>10.50 vol.%<br>$T_0 = 298.15 \text{ K}$<br>$p_0 = 1 \text{ atm}$ | $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$ | 8.80                              | 8.68   | 8.30                             |

<sup>a</sup> experimental data from (Razus et al., 2006) and (Cashdollar et al., 2000); <sup>b</sup> calculation data from (Razus et al., 2006)

The measurements by (Razus et al., 2006) were made starting at fuel concentrations near the LFL and using oxygen concentrations (from the air and nitrogen additions) that were near the LFL multiplied by the stoichiometric oxygen/fuel ratio as reported by Cashdollar et al. (2000). The oxygen concentration was varied in steps of 0.2 % until the marginal explosion conditions were delineated and verified. Then the fuel concentration was changed and the minimum oxygen concentration again determined. The process was repeated until a global maximum explosion pressure ( $p_{\max}$ ) with added N<sub>2</sub> was established.

### 4. Analysis

Present model computed adiabatic flame temperatures and adiabatic explosion pressures of C1-C3 alkane-air mixtures at various initial pressures were calculated, taking into account 26 species (H, H<sub>2</sub>, O, O<sub>2</sub>, HO<sub>2</sub>, H<sub>2</sub>O,

H<sub>2</sub>O<sub>2</sub>, OH, CO, CO<sub>2</sub>, CHO, CH<sub>3</sub>, CH<sub>2</sub>O, HCN, NO, N<sub>2</sub>O, NO<sub>2</sub>, CH<sub>2</sub>CO, NH<sub>2</sub>, HNO, C<sub>2</sub>N<sub>2</sub>, NH<sub>3</sub>, N<sub>2</sub>, CH<sub>2</sub>OH, C<sub>2</sub>H<sub>4</sub>, C) and assuming the thermodynamic equilibrium reached in the flame. Presented model is effective for C-H-N-O systems, at variable initial temperatures and/or initial pressures.

Element balanced equation:

$$a_j = \sum_{i=1}^l n_i A_{i,j} \quad (1)$$

where  $a_j$  are moles of j-th element (atom);  $n_i$  are moles of i-th species;  $A_{i,j}$  number of j-th element in i-th species;  $l$  is the number of elements;  $j$  is the number of species.

The free energy (Helmholtz function) of the system F equation:

$$F = \sum_{i=1}^l n_i f_i \quad (2)$$

where  $F$  is the free energy (Helmholtz function) of the system;  $n_i$  are moles of i-th species;  $f_i$  is free energy of i-th species.

$$f_i = \sum_{j=1}^J \lambda_j A_{i,j} \quad (3)$$

where  $f_i$  is free energy of i-th species;  $\lambda_j$  are the Lagrangian multipliers for each element ( $j = 1$  to  $J$ );  $A_{i,j}$  number of j-th element in i-th species.

$$g_i^\circ = \Delta H_f^\circ + (h_i - h_i^\circ) - T s_i^\circ \quad (4)$$

where  $g_i$  is the Gibbs free energy for single i-th species;  $\Delta H_f^\circ$  is the enthalpy of formation of the i-th species at standard conditions

$$f_i = g_i + RT \ln\left(\frac{n_i}{n}\right) + RT \ln\left(\frac{RT}{V}\right) \quad (5)$$

where  $g_i$  is the Gibbs free energy for single i-th species;  $R$  is the universal gas constant;  $T$  is temperature;  $n_i$  is the number of moles of every species;  $V$  is the volume.

$$a_j = n \sum_{i=1}^l A_{i,j} \exp\left(-g_i^\circ + \frac{1}{RT} \sum_{j=1}^J \lambda_j A_{i,j} - RT \ln \frac{RT}{V}\right) \quad (6)$$

where  $a_j$  are moles of j-th element (atom);  $n_i$  are moles of i-th species;  $A_{i,j}$  number of j-th element in i-th species;  $l$  is the number of elements;  $j$  is the number of species;  $g_i$  is the Gibbs free energy for single i-th species;  $\lambda_j$  are the Lagrangian multipliers for each element ( $j = 1$  to  $J$ );  $R$  is the universal gas constant;  $T$  is temperature;  $n_i$  is the number of moles of every species;  $V$  is the volume.

$$1 = \sum_{i=1}^l \exp\left(-g_i^\circ + \frac{1}{RT} \sum_{j=1}^J \lambda_j A_{i,j} - RT \ln \frac{RT}{V}\right) \quad (7)$$

where  $g_i$  is the Gibbs free energy for single i-th species;  $A_{i,j}$  number of j-th element in i-th species;  $l$  is the number of elements;  $\lambda_j$  are the Lagrangian multipliers for each element ( $j = 1$  to  $J$ );  $R$  is the universal gas constant;  $T$  is temperature;  $n_i$  is the number of moles of every species;  $V$  is the volume.

The set of non-linear Eqs(6-7) is solved by the use of the Newton-Raphson method. Known values of  $\lambda_j$  allow calculating the composition of the product  $x_i$ . The required solution is when  $F$  reaches a minimum for all species from 1 to  $l$ . The chemical equilibrium is reached when the Gibbs free energy is minimized (first part from Eqs(6-7) and if the mass balance of each element is conserved (second part of the Eqs(6-7)). Besides the energy balance also them as balance must be conserved for a closed system, the number of atoms of the elements must by the same for the initial and end state. At constant volume conditions the Helmholtz free energy needs to be minimized (Eqs(4-5)). Knowing the Gibbs or the Helmholtz energy at given temperature and pressure the chemical equilibrium is calculated, for each species, reactants and products, revealing its composition at the equilibrium state. The theory is described in (Reynolds, 1986).

## 5. Experiment

For binary premixed mixtures explosions the specific variant of stainless steel 1 m<sup>3</sup> sphere was used. With the strengthened 1 m<sup>3</sup> sphere it is possible to conduct experiments at final pressures not exceeding 20 bar, and initial temperatures, up to 200 °C. A fast acting system for homogenization of the liquid within an adjustable time, called the homogenization time. All parts are temperature controlled and thermally insulated. The

development of the explosion in the explosion chamber is monitored independently by two piezo-electrical pressure transducers. The partial pressure method was used for both gas/vapor mixtures preparation. Gases were supplied from compressed gas bottles. The adiabatic explosion pressures, computed by assuming chemical equilibrium within the flame front are examined in comparison with the measured explosion pressures.

## 6. Results and discussion

The element potential approach in the thermochemical equilibrium calculations applied in subroutine has been used for explosion pressure calculations. The chemical equilibrium model assumes adiabatic conditions in a constant volume, and formation of equilibrium defined concentrations of post explosion compounds and their expansion due to the temperature rise caused by the liberated heat. This approach represents ideal deflagrations in closed systems well and gives the highest possible attainable explosion pressures. The thermodynamics of gas mixtures as well as post-explosion products, at modest pressures, are described with sufficient accuracy by ideal gas behavior and ideal condensed phase products. Computed adiabatic flame temperatures and adiabatic explosion pressures for methane / hydrogen / air mixtures at various initial temperatures and ambient initial pressure are given in Table 2.

Table 2: Computed adiabatic flame temperatures and explosion pressures for propane-air mixtures, at  $T_0 = 298.15 \text{ K}$  and  $p_0 = 1 \text{ atm}$

| $T_{\text{init}}$<br>(K) | CH <sub>4</sub> (presented) |           | H <sub>2</sub> (presented) |           | CH <sub>4</sub> /H <sub>2</sub> (presented) |           |
|--------------------------|-----------------------------|-----------|----------------------------|-----------|---|-----------|
|                          | $p_{\text{max}}$ (bar)      | $T_f$ (K) | $p_{\text{max}}$ (bar)     | $T_f$ (K) | $p_{\text{max}}$ (bar)                      | $T_f$ (K) |
| 298 <sup>a</sup>         | 4.13                        | 1,232     | 2.04                       | 616       | 7.36  | 2,249     |
| 363 <sup>a</sup>         | 3.53                        | 1,282     | 1.84                       | 677       | 6.14  | 2,284     |
| 423 <sup>a</sup>         | 3.14                        | 1,329     | 1.71                       | 732       | 5.34  | 2,316     |
| 298 <sup>b</sup>         | 6.12                        | 1,824     | 2.80                       | 857       | 8.59  | 2,526     |
| 363 <sup>b</sup>         | 5.14                        | 1,867     | 2.45                       | 914       | 7.14  | 2,557     |
| 423 <sup>b</sup>         | 4.51                        | 1,908     | 2.23                       | 966       | 6.20  | 2,585     |
| 298 <sup>c</sup>         | 7.01                        | 2,087     | 3.17                       | 975       | 8.08  | 2,278     |
| 363 <sup>c</sup>         | 5.86                        | 2,126     | 2.75                       | 1,030     | 6.75  | 2,316     |
| 423 <sup>c</sup>         | 5.12                        | 2,162     | 2.48                       | 1,081     | 5.88  | 2,352     |

<sup>a</sup> methane (2.80 vol %), hydrogen (2.80 vol %), H<sub>2</sub>/CH<sub>4</sub> (5.60 vol %); <sup>b</sup> CH<sub>4</sub> (5.06 vol %), H<sub>2</sub> (5.06 vol %), H<sub>2</sub>/CH<sub>4</sub> (10.12 vol %); <sup>c</sup> methane (6.22 vol %), hydrogen (6.22 vol %), H<sub>2</sub>/CH<sub>4</sub> (12.48 vol %)

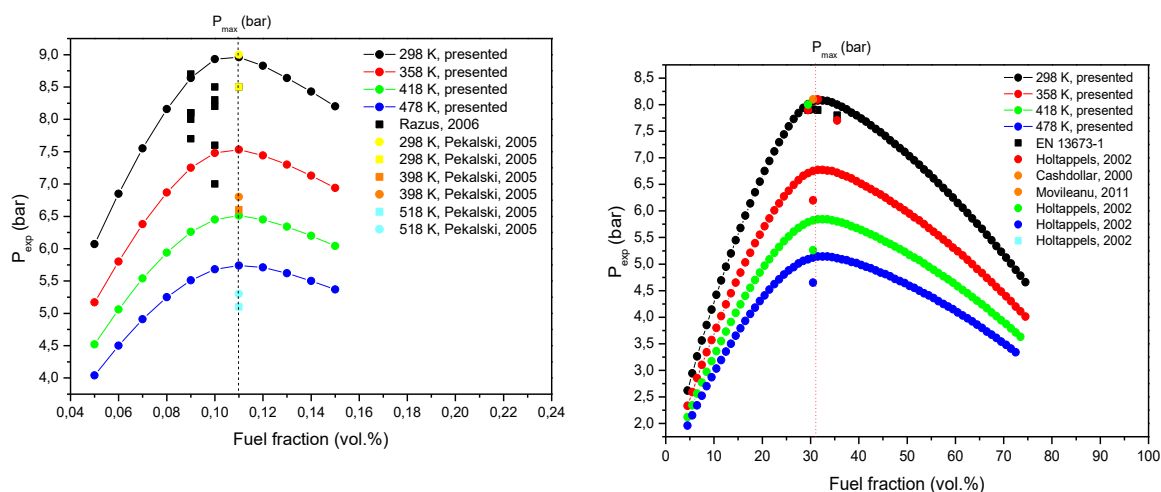


Figure 1: Calculated explosion pressure vs fuel fraction for explosions of a) CH<sub>4</sub>/O<sub>2</sub>/N<sub>2</sub> mixture at 298 K (top), 358 K (upper middle), 418 K (lower middle), and 478 K (bottom); b) H<sub>2</sub>/O<sub>2</sub>/N<sub>2</sub> 298 K (top), 358 K (upper middle), 418 K (lower middle), and 478 K (bottom)

The deviations between the adiabatic flame temperatures and between the adiabatic explosion pressures of fuel-air mixtures were calculated in various initial conditions with the presented model and two available programs range within -1.0 and +1.0 % and reveal the influence of thermophysical properties of significant

compounds (specific heats, standard formation enthalpies and standard entropies) on the calculated equilibrium parameters. The reported adiabatic flame temperatures and adiabatic explosion pressures show that presented model is adequate for equilibrium computations, applied to fuel-air mixtures in various initial conditions. Such differences explain also the deviations observed in  $T_{f,v}$  and  $p_{max}$ , calculated by GASEQ, for the other examined fuels. Since some species are predicted well and others not, it is therefore difficult to confirm, whether the equilibrium state was attained or not and the fuel could be partly oxidized.

Figure 1 shows maximum pressures computed for the stoichiometric  $CH_4/O_2/N_2$  and  $H_2/O_2/N_2$  mixture at various fuel fractions and various initial temperatures (298 K, 363 K, 423 K, 500 K). The shape of the explosion pressure curves with varying methane concentration is similar at all investigated initial temperatures. The maximum value of the explosion pressure is found at 11 mole % of methane for all conditions. As expected the increase in the initial temperature lowers the explosion pressure, and increases the flammability range. The upper explosion limit increases and the lower explosion limit decreases. When the mixture composition approaches the flammability limits the explosion pressure drops sharply to zero in all investigated cases. The calculated results show a reasonable agreement at the near stoichiometric concentrations with the results from (Kuchta, 1985), which was later confirmed by (Kondo et al. 2006, 2008).

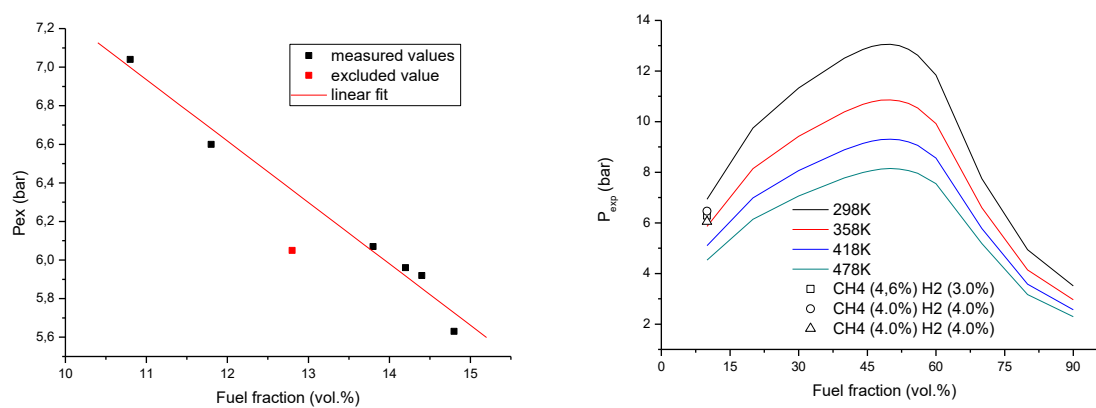


Figure 2: Explosion pressure vs fuel fraction for explosions of  $CH_4/H_2/O_2/N_2$  mixture a) at measured concentrations; b) at calculated and measured concentrations

## 7. Conclusions

Adiabatic flame temperatures and adiabatic explosion pressures of fuel-air mixtures at various initial temperatures were calculated. In the present study we accurate a theoretical calculation on maximum explosion pressure in closed vessel deflagration of stoichiometric gaseous mixtures, for standard temperature and we reported calculations for various initial temperatures within 20 °C - 250 °C for ambient initial pressure. Calculated explosion pressures assumed chemical equilibrium within the flame front. The influence of initial temperature on explosion pressure are presented for hydrogen and gaseous  $C_nH_{2n+2}$  ( $n=1-3$ ) + air/oxygen mixtures and the results are compared with the GASEQ calculations and with the experimental results. The explosion pressures should be always higher than the experimental values and that was observed for all fuel-air mixtures (in terms of comparison Table 1 and Figure 1). Thus the equilibrium calculations can be used as a rough calculation of a worst case scenario. The adiabatic explosion pressures  $H_2/CH_4/O_2/N_2$  mixture with air at various initial temperatures and pressures were calculated. The model predictions for the syngas mixtures are compared for four different initial temperatures. Although the results from the evaluation indicate that presented theoretical simulations can become a valuable tool for rough estimation, the modelling requires further improvements to be useful for consequence modelling and design of industrial facilities. Thus, at the first stage, the equilibrium calculations can be used as a rough calculation of a worst case scenario. At the same time, these values will be used as approximate initial values for explosion experiments carried out in heated 1 m<sup>3</sup> explosion apparatus designed by OZM Research s.r.o. at Energy Research Centre, VŠB - Technical University of Ostrava. The results represent a continuation of numerous efforts by various research groups, where the key underlying problem has been the understanding of results obtained in laboratory tests for predicting the consequences of multicomponent gas mixture explosion scenarios in industry (Skřinský et al. 2015), which are in agreement with other publications of the authors collective (Skřinská et al., 2014a, 2014b).

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