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Explosion Characteristics of Methane at Low and Elevated Initial Temperatures

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In the millisecond time domain, deflagration curves of the methane, CH_4, have been observed at low and elevated initial temperatures. 20-L closed spherical chamber have been adopted for low and high initial temperatures measurements. Methane air mixtures were studied experimentally and numerically for different equivalence ratios between 0.2 and 2.5 and initial temperatures of -20, -10, 0, 10, 20, 30, 40, 50 °C. More than three hundred pressure-time curves were recorded. Twenty-five deflagration curves of the CH_4 have been observed in the below-zero temperature region in 20-L volume for the first time, including two pressure-time curves in -20 °C. The effects of temperature on the maximum explosion pressure, maximum rate of pressure rise, and deflagration index were investigated. The evaluated experiments' actual results are the maximum pressure rise rate for -20 °C. Our results should also provide critical information applicable to thermodynamic and kinetic modeling of methane explosion and flame low-temperature chemistry. This work allowed a systematic comparison of the structural and bonding properties among the C_nH_{2n} analogs in the physics and chemistry of low temperatures explosions.

1. Introduction

Many scientists have studied the explosion characteristics of combustible gases from which methane is the most pronounced. The initial conditions in the experiments were predominantly atmospheric pressure and room temperature. While the studies at ambient and elevated initial temperatures are well established, the investigation at low initial temperatures is relatively scarce. Karim et al. (1984) investigated the lean flammability limits in the air of methane, hydrogen, and carbon monoxide at low temperatures. A circular stainless-steel tube approximately 50 mm in diameter and just over 1 m in length uniformly cooled by circulating liquid nitrogen was used. Wierzba et al. (1990) reported some experimentally determined rich flammability limits in the air of methane, ethane, propane, butane, propylene, and ethylene obtained at initial temperatures extending down to -60 °C in a specially designed stainless steel smooth circular tube of 50 mm diameter that was just over one meter in length. Wierzba et al. (1992) published the rich flammability limits in the air of hydrogen at atmospheric pressure. For upward flame, propagation was established consistently under initial isothermal conditions at low temperatures extending to -60 °C. The lower explosion limits were determined down to -100 °C. Li et al. (2011) The flammability limits of methane/nitrogen mixtures in the air were measured in a vertical stainless-steel cylinder at atmospheric pressure and a wide temperature range of 150-300 K. Cui et al. (2016) published the experimental study of flammability limits of methane/air mixtures at a wide temperature range 123-273 K and a pressure range from 0.1-0.9 MPa. The explosion vessel was a vertical stainless-steel cylinder with a height of 300 mm, an inner diameter of 100 mm, and a wall thickness of 25 mm. Cui et al. (2018) measured the explosion characteristics of a methane-air mixture at low initial temperatures and elevated pressures in stainless steel with an inner diameter of 100 mm and a height of 300 mm for the initial temperature range of 123–273 K. Pio et al. (2018) presented a numerical study for the temperature of 250–325 K and composition 0.4–2.5 on the laminar burning velocity and flammability limits of sour gas (CH_4 - H_2S - Air mixture). Pio et al. (2019) studied the effect of ultra-low temperature 200–300 K on the laminar burning velocity, flammability limits, and the limiting oxygen concentration of methane/air/diluent mixtures limiting oxygen concentration on a detailed kinetic mechanism.

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2. Experimental set-up

2.1 Explosion vessel

The experiments were performed in a constant volume stainless steel double wall vessel of spherical shape (SN: 497-OZM-15, OZM Research, s.r.o.) adopted from the standard (Skrinsky, 2018) to the presented low and high-temperature experiments by the additional agitator. The set-up consists of an explosion vessel, temperature control unit, spark generator, vacuum pump, and data acquisition system.

2.2 Heating and cooling of the vessel

Digitally adjustable temperature control device Presto (SN: 10291377, JULABO GmbH, model A 30) has been used to heat and cool the oil in the instrument to the specified temperature close to the expected. A temperature control system has been used as a regulating system of the vessel from -20 °C up to 60 °C. The temperature ranged from -20 °C to 60 °C, with a temperature fluctuation of less than 2 °C. The initial temperature at the ignition time has been measured using the calibrated thermocouple (SN: 10291377, Jakar) with an accuracy of 0.5 °C located on the top of the explosion vessel.

2.3 Spark generator

The electric discharge ignited the mixture from a permanent spark generator (15 kV, AC 20 mA) with an ignition delay time of 85 ms to have relevant data for future comparison with measurements applying chemical igniters (25 ms dispersion + 60 ms ignition delay). The rods of the electrodes were positioned in the center of the testing vessel with a distance between the tips of 5 mm. The spark discharge time was adjusted to 200 ms.

2.4 Pressure measuring unit

The dynamic explosion pressures have been recorded by pair of piezoelectric quartz pressure sensors (SN: 4512821 and SN: 4512822, Kistler, model 701A) and with a transducer sensor charge amplifier (Kistler, model 5041E1). The operating temperature range of the sensors is from -150 °C to 200 °C, which is satisfactory for the presented experiments. The calibrated partial range for the sensors was from 0 bar to 20 bar.

2.5 Data acquisition

The data acquisition system comprises the pressure sensors, transducer sensors, signal conditioning system, and signals converter system connected to the PC. The signal conditioning module (Media, model UDAQ-3644) has worked at a sampling frequency of 50 000 Hz and a sampling period of 0.02 ms with a high-resolution 16-bit A/D converter connected to the PC´s USB. The user interface controls the acquisition (PROMOTIC system, MICROSYS, s.r.o).

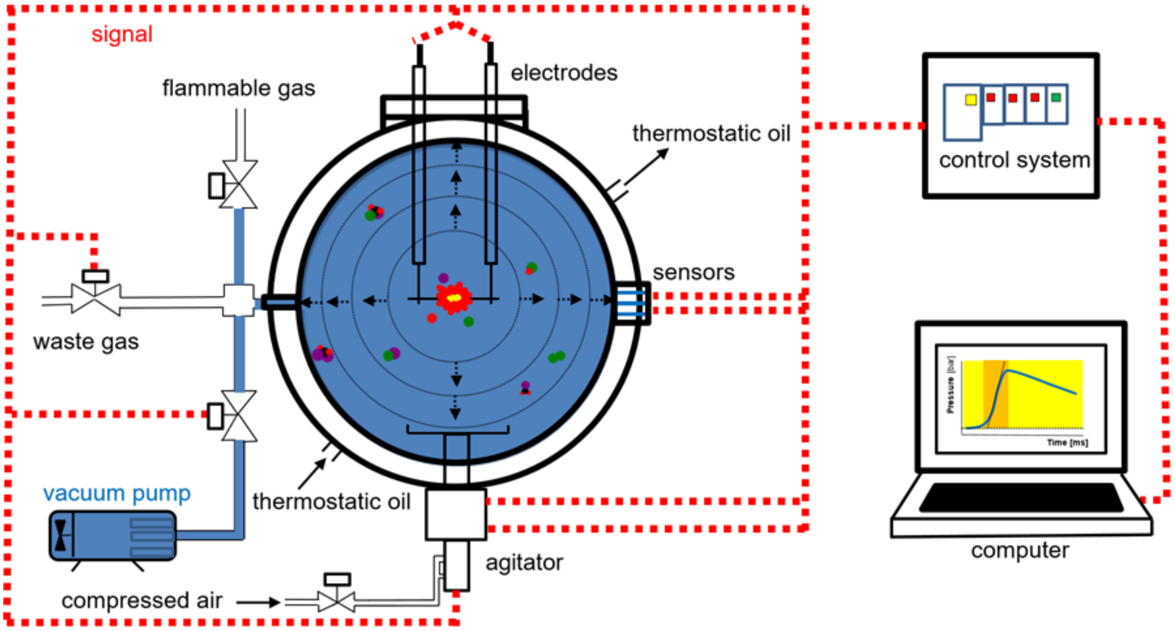

Figure 1: Experimental set-up

2.6 Experimental procedure

The methodology is applied to investigate the explosion severity, and sensitivity characteristics are based upon the European Standard EN 15967 (2012). This method allows the measurement at atmospheric conditions and has been adapted for high and low-temperature studies. The maximum explosion pressure is determined during measurements of the explosion pressure by varying stepwise the content of flammable gas in the mix until the maximum value is found.

2.7 Experimental uncertainty

The explosion parameters' uncertainty mainly arises from the methane content measurements by a partial pressure method, the initial temperature measurements, and the initial pressure measurements. The methane, oxygen, and nitrogen purities were more significant than 99.95 %. All chemicals were commercial products from Siad a.s. The initial pressure was measured using a precision pressure gauge of 0.02 % and a 0–16 bar pressure range. Therefore, the initial pressure measurements have a maximum error of ±3.2 mbar. The initial temperature is measured using a fast response thermocouple FLEXITEMP 60 (SN: 3013271, Jakar) with an accuracy of 0.5 % and in the temperature range -250-450 °C. Therefore, the initial temperature measurements have a maximum error of ±6.0 °C for 1200 °C and ±1.3 °C for -250 °C and in the investigated temperature range ±0.1 °C for -20 °C and ±0.3 °C for +60 °C. A static pressure gauge measured the initial pressure.

3. Calculation procedure

To reduce the number of experimental tests, preliminary thermodynamic and kinetic analyses were performed to predict the fuel-air equivalence ratio resulting in maximum pressure. The calculation procedure included both the physical and the chemical parts.

Physical part:

Figure 2 and Equation 1 describe the model for the moving flame front during a closed vessel deflagration. Assuming that the flame thickness is negligible concerning the vessel radius, the burning velocity is similar in all volumes. The point ignition occurs at the center of the vessels.

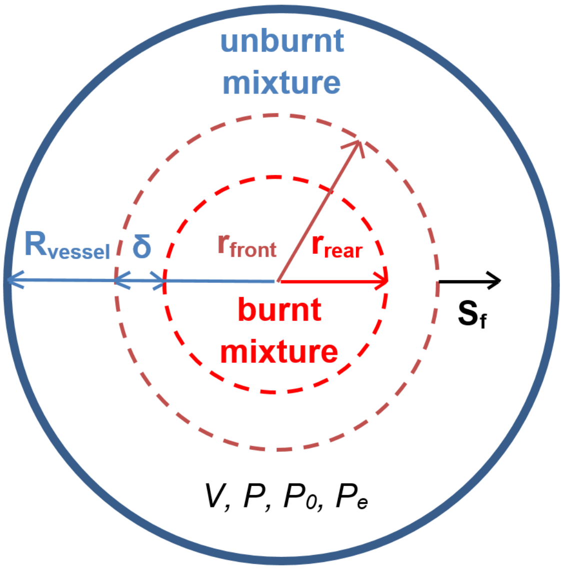

Figure 2: Flame front diameter calculation

$$r_{front} = \left(\frac{3.\delta.V}{\pi}\cdot\left[1-\left(\frac{P_0}{P}\right)^{\frac{1}{\gamma}}\cdot\frac{P_e-P}{P_e-P_0}\right]\right)^{\frac{1}{4}} \quad (1)$$

Chemical part:

The knowledge of the chemical equilibrium composition of a studied chemical system permits the calculation of theoretical thermodynamic properties for the system. The calculation procedure is based on the minimization of Gibbs Free Energy (GFE) in Equation 2.

The GFE of the mixture at pressure p is given by:

$$\frac{G}{RT} = \sum_{i=1}^{nSp} \left(\frac{x_i G_i^0}{RT} + x_i \ln \frac{x_i}{\sum x_i} + x_i \ln p \right) \tag{2}$$

4. Results and discussion

4.1 Calculations

The maximum explosion pressure is an essential indicator for evaluating explosion energy distribution. The normalized maximum explosion pressures for various initial temperatures and concentrations are presented in Figure 3.

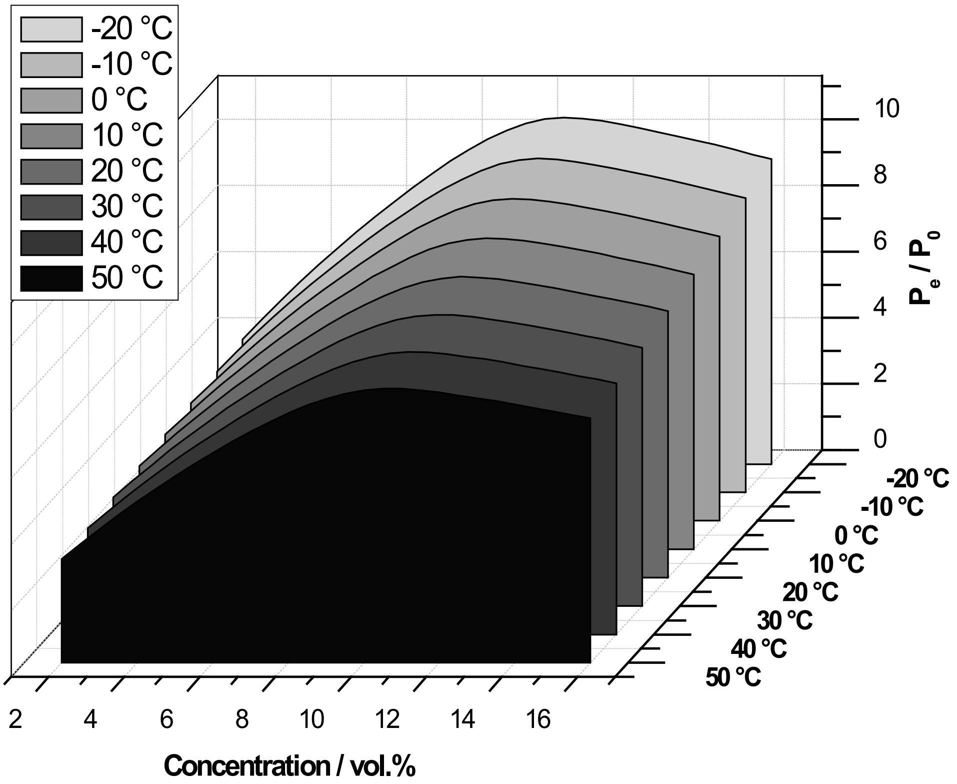

Figure 3 shows that when the gas concentration is constant, the explosion pressure increases with the temperature decrease. When the gas concentration is close to stoichiometric, the maximum explosion pressures at 50, 40, 30, 20, 10, 0, -10, and -20 °C are relatively different.

4.2 Experiment

Figure 4 gives the selected results to demonstrate the effect of different initial temperatures on the explosion pressure and the pressure rise rate during the explosion process. The explosion and adiabatic equilibrium pressure are normalized concerning the initial pressure ($p_0 = 101$ kPa).

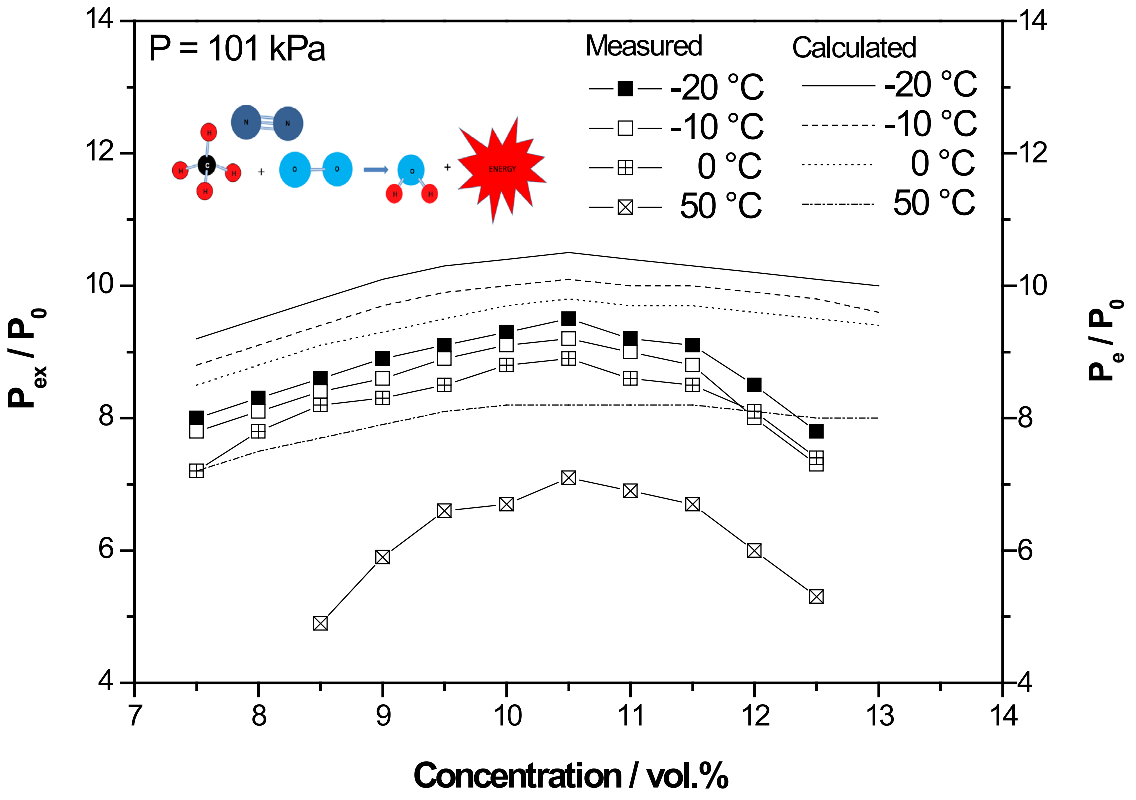

Figure 4: P_{ex}/P_0 versus equivalence ratio for methane

In the presented study, the measured maximum explosion pressure of stoichiometric methane-air is 10.0 bar, lower than the calculated adiabatic explosion pressure of 10.5 bar. This is attributed to the energy loss of the walls. Each test was repeated three times to obtain appropriately averaged results, and the average was plotted in the pressure-time curve.

5. Conclusions

The explosion behavior of methane-air mixtures with the different gas compositions was experimentally and numerically studied at the specific initial temperature explosion conditions in a closed spherical explosion chamber at Energy Research Centre, VSB-TU Ostrava. An employed method combines the preliminary thermo-kinetic chemical equilibrium study to identify the specific concentrations to be further experimentally analyzed, thus substantially reducing the number of experimental tests. The presented results allow us to experimentally quantify the effect of different initial temperatures on the pure gas-air explosion parameter – the maximum explosion pressure. The main conclusions are summarized as follows:

1) Determination of maximum explosion pressure of methane-air mixtures at temperatures of T = -20 - 60 °C and concentrations = 2.5 - 16.0 vol.%.
2) Explosion pressure of the methane-air mixture reaches maximum values near the stoichiometric concentration with a concentration = 10.5 vol.% within the studied range, i.e., 2.5 - 10.5 at temperatures of -20 - 60 °C.
3) The explosion pressure varied between 10.5 to 8.3 bars, for initial temperatures -20 - 60 °C is behind the 10 % experimental error.

Nomenclature

δ – flame thickness, m
G – Gibbs Free Energy, J/kg
K_G – deflagration index, bar.m/s
n_{sp} – number of species, -
p – pressure, bar
p_e – explosion pressure, bar
p_0 – initial pressure, bar
R – universal gas constant, J/K.mol
r_{front} – flame front at the unburnt mixture, m
r_{rear} – flame front at the burnt mixture, m
st – stoichiometric conditions, -
t – time, s
φ – fuel-air equivalence ratio, -
T – temperature, K
V – vessel volume, m^3
x – number of moles in the mixture, mol

References

Karim G.A., Wierzba I., Boon S., The lean flammability limits in the air of methane, hydrogen and carbon monoxide at low temperatures, 1984, Cryogenics, 305-308.

Wierzba I., Harris K., Karim G. A., Effect of low temperature on the rich flammability limits of some gaseous fuels and their mixtures, 1990, Journal of Hazardous Materials, 257-265.

Wierzba I., Harris K., Karim G. A., Effect of low temperature on the rich flammability limits in the air of hydrogen and some fuel mixtures containing hydrogen, 1992, International Journal of Hydrogen Energy, 149-152.

Li Z., Gong M., Sun E., Wu J., Zhou Y., Effect of low temperature on the flammability limits of methane/nitrogen mixtures, 2011, Energy, 5521-5524.

Cui G., Li Z., Yang Ch., Experimental study of flammability limits of methane/air mixtures at low temperatures and elevated pressures, 2016, Fuel, 1074-1080.

Pio G., Palma V., Salzano E., A numerical study on the effect of temperature and composition on the flammability of sour gas, 2018, Joint meeting the German and Italian sections of the combustion institute, 1-7.

Pio G., Salzano E., The effect of ultra-low temperature on the flammability limits of a methane/air/diluent mixtures, 2019, Journal of Hazardous Materials, 224-229.

EN 15967, Determination of the maximum explosion pressure and the maximum rate of pressure rise of gases and vapors, 2012.

Skřínský J., Ochodek, T., Explosion Characteristics of Propanol Isomer–Air Mixtures, 2019, Energies, 1574.