IChemE
www.icheme.org/journals
doi: 10.1205/psep.04211

0957–5820/05/$30.00+0.00

Trans IChemE, Part B, September 2005
Process Safety and Environmental Protection, 83(B5): 421–429

DETERMINATION OF THE EXPLOSION BEHAVIOUR OF METHANE AND PROPENE IN AIR OR OXYGEN AT STANDARD AND ELEVATED CONDITIONS

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The article reports on the explosion pressure data for methane-air, and propene-air and -oxygen mixtures over their entire flammable range at standard and elevated pressure and/or temperature from experiments conducted in a 20-litre explosion vessel. The initial temperatures are 20, 120 and 240°C and the initial pressures are 1, 5 and 10 bara. The explosions are classified into three combustion conversion regimes based on the shape of the pressure time traces. The experimental results are compared to chemical equilibrium calculations. Four thermodynamic models, with different constraints on soot formation, are used to calculate the explosion pressure. The discrepancy between the results of experiment and calculation mirrors the degree of conversion of the initial mixture and the degree the explosion can be considered adiabatic. Efforts were made to identify the main cause of the large discrepancy in two of the combustion regimes. Soot formation is found to be an important parameter affecting explosion pressure.

Keywords: hydrocarbon; gas explosion; pressure; thermodynamic equilibrium.

INTRODUCTION

Gas explosion severity parameters are the explosion pressure, P_{exp}, defined as the highest pressure reached during an explosion in a closed volume at a given fuel concentration, and the maximum explosion pressure, P_{max}, found as the highest P_{exp} over the flammable range. These are needed for risk assessment, pressure vessel design for explosion containment and design of pressure relief systems.

Few data at standard conditions are available in open literature. Many processes, especially in the petrochemical industry, however, operate at elevated temperature and pressure. While the values of such explosion parameters at these elevated conditions are essential to safety and reliable operation, they are nevertheless largely unavailable in open literature.

Here, experimental data are presented of methane-air mixtures at standard and elevated conditions as well as of propene-air or -oxygen mixtures at standard and elevated pressure. Additionally, with several thermodynamic models explosion pressures are calculated, compared to the experimental ones and differences explained.

EXPERIMENTAL APPARATUS

Two experimental set-ups were used. For methane-air explosions the Delft strengthened stainless steel 20-litre sphere presented in Figure 1 was used. The dimensions of the equipment are identical to the standard 20-litre sphere (ASTM E1226-94, 1994; ISO 6184-2, 1985). With the strengthened 20-litre sphere it is possible to conduct experiments at final pressures not exceeding 200 bar, and initial temperatures, up to 300°C. The explosion chamber is connected to a storage canister through a duct. A fast acting valve opens and closes the borehole of the duct within an adjustable time, called the injection 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. Furthermore a total of six thermocouples, three horizontal and three vertical, are placed inside the sphere at equal distances from each other and the wall. All data are recorded by computer. Between the two electrodes, a tungsten fused wire is placed, generating an ignition energy of 3.5 J. The partial pressure method was used for

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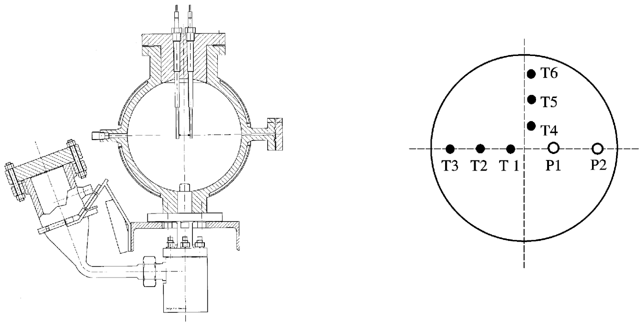

Figure 1. Cross-section of the strengthened 20-litre sphere (left) and location of thermocouples (right).

mixture preparation with a high accuracy pressure manometer of 2 millibar (Ruska 7000). Air was supplied from compressed gas bottles.

Determination of the explosion pressures of propene-air and propene-oxygen mixtures were done in another explosion vessel of similar dimensions at BASF Ludwigshafen. This vessel can be heated up to 500°C and has a design pressure of 1200 bar (static pressure) at 500°C. The vessel is not equipped with a rapid injection system. The mixtures were ignited in the centre of the vessel by a nichrome fused wire with the ignition energy of 20 J.

COMPUTATIONAL APPROACH

The element potential approach in the thermochemical equilibrium calculations applied in the Chemkin 3.6.2 subroutine (http://www.reactiondesign.com/lobby/open/index.html) has been used for explosion pressure calculations. The chemical equilibrium model assumes adiabatic conditions in 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 assuming ideal gas behaviour and ideal condensed phase products. This approach represents 'ideal' deflagrations in closed systems well and gives the highest possible attainable explosion pressures.

Methane-air explosion pressures are calculated using the species and their thermodynamic values from the GRI 3.0 (http://www.me.berkeley.edu/gri_mech/version30/text30.html) and the Konnov 5.0 (http://homepages.vub.ac.be/~akonnov/science/mechanism/version0_5.html) mechanisms. The latter is also used for both propene-air and propene-oxygen explosion calculations.

In order to study soot formation, several mechanisms are combined. To the above, higher aromatic compounds are added from a mechanism developed for soot formation (Appel *et al.*, 2000) at elevated pressure. These soot species are aromatic compounds consisting of up to seven benzene rings. Soot is also represented by solid phase carbon in the form of graphite C(S) (Pekalski *et al.*, 2002). Consequently four sub-models are used in this study. Model A has no solid carbon nor aromatic compounds. Model B only considers aromatic compounds. Model C includes both, and model D only solid carbon. There were no noticeable differences between these models for calculation of explosion pressure of methane-air mixtures in the investigated range. More details are given elsewhere (Pekalski *et al.*, 2004).

RESULTS

Methane-Air Explosions

For methane-air explosion pressure calculations, for all conditions, there is no noticeable difference between results obtained from the GRI and the Konnov mechanisms, besides their differences in the species considered. The relative difference between the results from these two models is below 0.08%. Additionally, at all conditions investigated, inclusion of solid carbon or aromatic species does not significantly affect the explosion pressure within the range studied. An insignificant difference, with a relative error below 0.6%, exists between the models with soot and models without soot. The highest error occurs at very fuel rich conditions (CH4 of 28–30%), in all other cases the error is a magnitude lower.

Methane air explosions at standard conditions—comparison with existing data

Experimental results obtained in this study are first compared to already published results (Cashdollar and Hertzberg, 1985; Kuchta, 2002; Mashuga, 1999; Dahoe, 2000) and presented in Figure 2. All experiments were performed in 20-litre spherical explosion vessels with ignition in the centre of the vessel. Besides one measurement of Cashdollar at 14 mole% of methane all results overlap each other within a tolerable experimental error. The $P_{\max}$ values are 8.3, 8.5, 8.2, 8.8 and 8.5 bara, respectively. According to the EC standard the maximum explosion pressure is found at 10.5 ± 0.5% methane in air with a value of 8.3 ± 0.3 bara (EN 13673-1, 2003).

Methane air at elevated conditions

The experimental and calculated explosion pressures of methane-air mixtures at one atmosphere and three different initial temperatures: 20, 120 and 240°C are presented in Figure 3.

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. The maximum explosion pressure is 8.5, 6.6 and 5.1 bara at 20, 120 and 240°C, respectively. The increase in the initial temperature lowers the explosion pressure, and

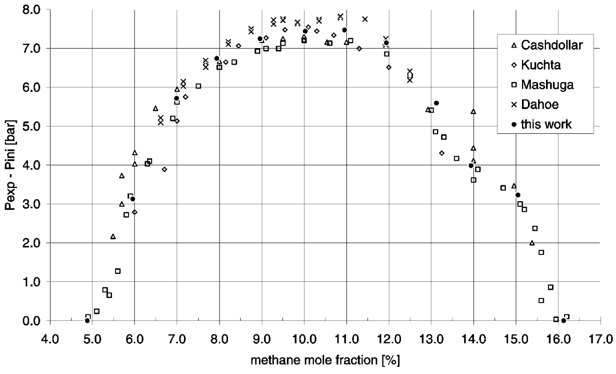

Figure 2. Experimental explosion pressures of quiescent methane-air mixtures over the flammable range at standard conditions (25°C and 1 atm).