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Experimental study of the pressure and temperature dependence on the upper flammability limit of methane/air mixtures

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Abstract

The flammability limits of methane/air mixtures are investigated experimentally at pressures up to 5500 kPa and temperatures up to 200°C. Two different criteria based on the maximum explosion pressure are used to define the flammability limit, the tangent criterion and the min–max criterion. It is shown that the min–max criterion should be used to determine the upper flammability limit (UFL), because the tangent criterion underestimates the UFL at initial pressures higher than ambient. In the pressure–temperature range tested second order pressure dependences and linear temperature dependences of the UFL are found. The temperature dependence of the UFL is influenced by the initial pressure which is in contrast with previous findings. © 1997 Elsevier Science B.V.

Keywords: Flammability limits; Methane/air mixtures; Combustion processes

1. Introduction

Combustible gases are frequently used in chemical processes. In order to evaluate the explosion hazards involved and to ensure safe and optimized operation of these processes, it is necessary to know the combustion characteristics under the working conditions, i.e. temperature and pressure.

At this moment, no numerical model is capable of predicting the flammability limits in all circumstances. Therefore, experiments still have to be performed. At ambient

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temperature and atmospheric pressure, these limits are well established [1–3]. On the other hand, at elevated temperatures and pressures only a limited number of data is available [3–5]. Moreover, the results of different investigators are sometimes contradictory.

The aims of the present work are (1) to determine experimentally the upper flammability limit of methane/air mixtures at pressures up to 5500 kPa and temperatures up to 200°C, and (2) to obtain a better understanding of the combustion processes near the upper flammability limit.

2. Experimental apparatus and procedure

The experimental apparatus is shown in Fig. 1. It consists of a closed spherical reaction vessel of 8 dm^3, which is large enough to neglect the influence of wall-quenching [3,4]. The vessel is designed to withstand explosion pressures up to 350 MPa at a temperature of 350°C.

Thermal mass flow controllers are used to control the flow rates of the different components of the gas mixture, i.e. methane and air. The separate gas flows are mixed and led through a static mixing chamber to ensure homogeneity. The total volume of the vessel is evacuated and then flushed with the gas mixture at least 10 times. The desired initial pressure of the gas mixture is achieved by controlling the flow with the in- and outlet valves. A thermostatically controlled electric heater which allows temperature control within 1 C is fitted around the vessel. The gas mixture is allowed to come to rest and equilibrate in temperature and pressure before each test. Before ignition, a gas-sample is taken for analysis by gas chromatography which ensures a relative accuracy of 0.5% in the determination of the composition of the mixture. The explosion vessel is opened after each test to investigate its contents, and sometimes the presence of soot was

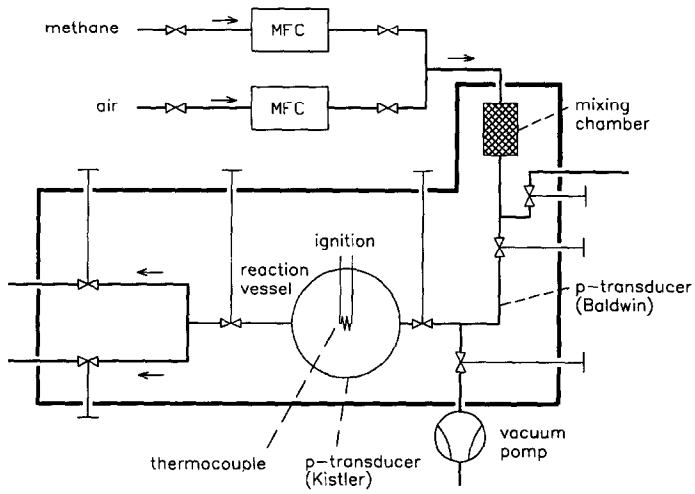

Fig. 1. Experimental apparatus.

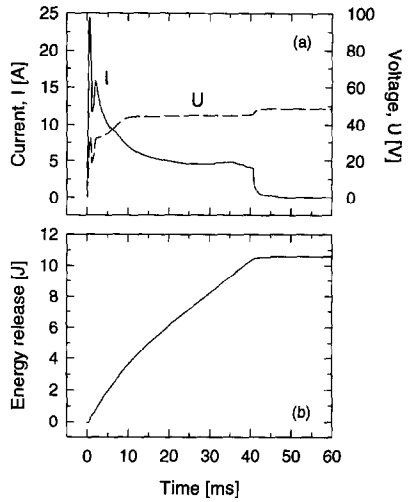

Fig. 2. Recorded current and voltage histories (a) and the calculated energy release (b) by fusing a spiral tungsten wire.

observed. Based on visual observation, three categories of soot formation are differentiated: no soot, little soot, and soot.

The initial pressure is measured with a resistive pressure transducer (Baldwin). The pressure and temperature histories during explosion are measured with a piezo-electric pressure transducer (KISTLER 601H or 603B) and one Cr/Al thermocouple positioned at the centre of the vessel, respectively.

Ignition is achieved by fusing a spiral tungsten wire, placed at the centre of the vessel. Such an igniter releases about 10 J in 0.040 s. This is illustrated in Fig. 2, which shows the current and the voltage recorded during a test (a), and the energy calculated from these recordings (b). It should be noted that the energy delivered by fusing a wire did not depend on the initial pressure and temperature.

The occurrence of an explosion is judged from the temperature and pressure histories. When a temperature increase of 2°C or a pressure increase of 1% is recorded, the attempt is called successful. When no temperature and pressure increase is observed, the attempt is called unsuccessful.

In the literature, different criteria are found to define a flammability limit. Fig. 3 illustrates two criteria that are used in this study: the tangent criterion (a) and the

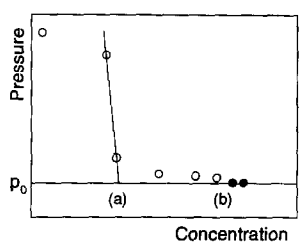

Fig. 3. The tangent (a) and the min–max criterion (b) which are used to define the flammability limit.

min–max criterion (b). The tangent criterion defines the flammability limit as the concentration where the steepest line between two successive points intersects the initial pressure line. The min–max criterion defines the upper flammability limit as the average between the highest flammable concentration and the lowest non-flammable concentration and the lower flammability limit as the average between the lowest flammable concentration and the highest non-flammable concentration.

3. Experimental results and discussion

3.1. Flammable region at 100 kPa and at 20°C

The data plotted in Fig. 4 is the result of tests on methane/air mixtures at ambient pressure and temperature. It shows the maximum explosion pressure as function of the methane concentration. The results obtained in this study are marked with (○) for a successful and with (●) for an unsuccessful attempt. Those are compared with the previously obtained results of Claessen et al. [5], with the results of Bartknecht [3] and with the recently published results of Checkel et al. [6]. The similarity between the different results proves the reliability of the experimental apparatus used.

The flammability limits of a methane/air mixture at 100 kPa and 20°C are found to be 4.6 ± 0.3% (vol.) and 15.8 ± 0.4% (vol.) using the tangent criterion and 4.6 ± 0.3% (vol.) and 15.7 ± 0.3% (vol.) using the min–max criterion for the LFL and the UFL, respectively. These values are almost similar to those reported by Müller [4] (4.7% and 16.1%) and by Berthold and Conrad [7] (4.5% and 16.2%) eventhough the test conditions were different.

3.2. Flammable region at 1000 kPa and at 20°C

In Fig. 5, the flammable regions at 100 and at 1000 kPa, both at 20°C, are plotted. As expected, the ratios between maximum explosion pressure, p_{ex}, and initial pressure, p_1, are almost equal at stoichiometric methane concentration (9.5%), and the flammable region widens with increasing initial pressures. Further, as can be seen in Fig. 5, the behaviour of the maximum explosion pressure ratio, p_{ex}/p_1, near the LFL is the same for both initial pressures. On the other hand, an important discrepancy is seen near the

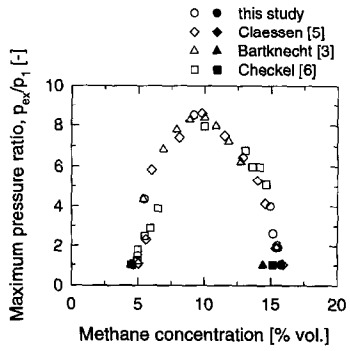

Fig. 4. Maximum explosion pressure ratios for methane/air mixtures ignited at 20°C and at 100 kPa.

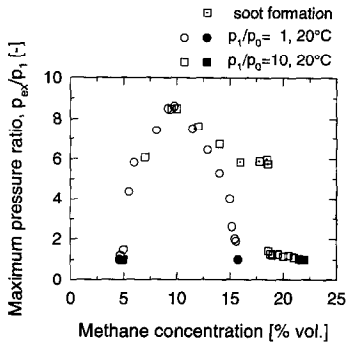

Fig. 5. Maximum explosion pressure ratios for methane/air mixtures ignited at 20°C and at 100 kPa and 1000 kPa.

UFL. At 1000 kPa a soot-zone and a twilight-zone are observed. Soot formation was observed between 16.0% and 18.6% methane (marked with (□)), and in this zone, the explosion pressure ratio reaches a plateau at a value of 6. In the twilight-zone, the explosion pressure ratio is rather small; it starts at 1.5 for a 18.7% methane concentration and reaches unity for a 21.7% methane concentration. Between these zones, the explosion pressure ratio drops very rapidly for a small increase of 0.1% in methane concentration.

The upper flammability limit is found to be $18.7 \pm 0.2\%$ (vol.) using the tangent criterion and $21.7 \pm 0.4\%$ (vol.) using the min–max criterion. The former value agrees well with the one reported by Müller [4] (18.2%), who used the tangent criterion.

Due to the significant difference between the two criteria, the min–max criterion should be preferred to define the UFL: the tangent criterion underestimates the UFL and neglects the twilight-zone. Disregarding the twilight-zone could lead to dangerous situations because the twilight-zone is characterized by a small but not negligible maximum explosion pressure ratio.

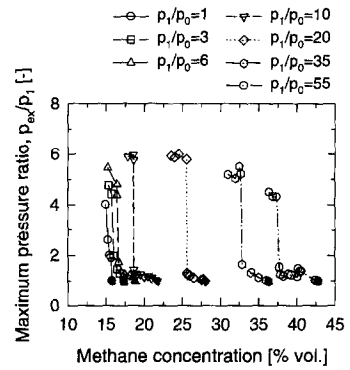

Fig. 6. Maximum explosion pressure ratios for methane/air mixtures ignited at 20°C and at various initial pressures.

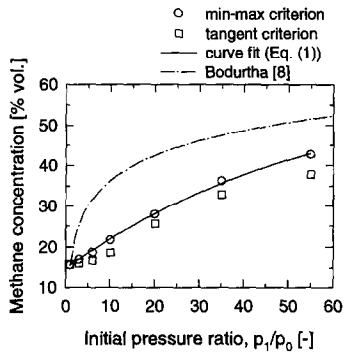

Fig. 7. Pressure dependence of the upper flammability limit for methane/air mixtures ignited at 20°C.

3.3. Pressure dependence of the upper flammability limit at 20°C

The measured maximum explosion pressure ratios for methane in air near the upper flammability limit at 20°C are shown in Fig. 6 for various initial pressures p_1. With increasing initial pressure there is not only, as expected, a widening of the flammability region, but also a widening of the twilight-zone.

Both the tangent and the min–max criteria are applied to the data shown in Fig. 6 to calculate the UFL at various initial pressures. The result is shown in Fig. 7. A second order curve fit is drawn through the data obtained by the min–max criterion giving the equation:

$$\mathrm{UFL}(p_1) = \mathrm{UFL}(p_0)\left[1 + a\left(\frac{p_1}{p_0} - 1\right) + \left(\frac{p_1}{p_0} - 1\right)^2\right] \tag{1}$$

with the following coefficients: $a = 0.0466$ and $b = -0.000269$.

In literature [2,8,9], a logarithmic pressure dependence of the UFL is suggested. The dashed-dot line in Fig. 7 corresponds with the relation given by Bodurtha [8]:

$$\mathrm{UFL}(p_1) = \mathrm{UFL}(p_0) + 20.6\log_{10}(p_1/p_0) \tag{2}$$

This expression is based on experimental data for the UFL of natural gas/air mixtures at

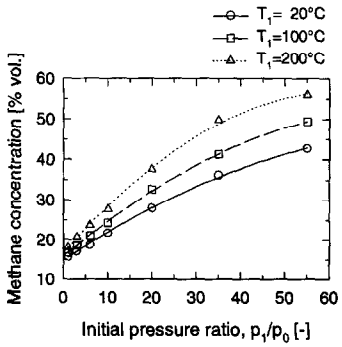

Fig. 8. Pressure dependence of the upper flammability limit for methane/air mixtures ignited at elevated temperatures.

Table 1
Coefficients of Eq. (1)

p_1 [°C]	UFL (p_0) [%]	a [−]	b [−]
20	15.7	0.0466	−0.000269
100	16.8	0.0552	−0.000357
200	18.1	0.0683	−0.000541

high pressures [9]. In the pressure range considered in the present work, this relation predicts too large values for the UFL of methane/air mixtures.

3.4. Pressure dependence of the upper flammability limit at elevated temperatures

To determine the pressure dependence of the upper flammability limit at elevated temperatures, additional experiments were performed at 100°C and at 200°C. The data obtained using the min–max criterion is shown in Fig. 8: higher initial temperature results in higher UFL, but the increase in the UFL depends on the initial pressure. The coefficients of the second order curve fits (see Eq. (1)) drawn through the different data, are given in Table 1.

3.5. Temperature dependence of the upper flammability limit at various initial pressures

Fig. 9 shows the upper flammability limit obtained by the min–max criterion as function of the initial temperature T_1. Through the data, straight lines are drawn using the equation:

$$\mathrm{UFL}(T_1) = \mathrm{UFL}(T_0)\left[1 + c\left(\frac{T_1 - T_0}{100}\right)\right] \tag{3}$$

Values for UFL (T_0) and c are given in Table 2 for various initial pressure ratios. Note that c gives the increase in UFL per 100°C temperature increase.

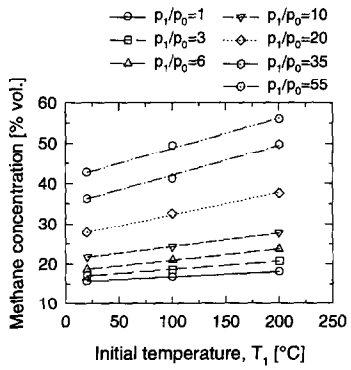

Fig. 9. Temperature dependence of the upper flammability limit for methane/air mixtures at various initial pressure ratios.

Table 2
Coefficients of Eq. (3)

p_1 / p_0 [−]	UFL (T_0) [%]	c [1/K]
1	15.7	0.0854
3	16.1	0.1157
6	16.6	0.1494
10	18.6	0.1530
20	25.6	0.1968
35	32.5	0.2033
55	37.8	0.1769

At atmospheric pressure c equals 8.5% which is almost similar to what is found in literature; Müller [4] suggests using $c = 8.7\%$ while Berthold and Conrad [7] suggest using $c = 8.1\%$. Increasing the initial pressure results in higher values for c, which confirms the conclusion that the temperature dependence of the UFL depends on the initial pressure.

3.6. Soot and twilight-zone

As mentioned above, sometimes two remarkable phenomena were observed near the upper flammability limit: soot formation just before the tangent criterion and an area between the tangent and the min–max criterion which is called the twilight-zone.

Fig. 10 shows the initial conditions at which soot, little soot and no soot formation was observed. From this figure, it can be seen that the initial pressures at which soot is formed have the tendency to decrease with increasing initial temperatures. Note that no soot was observed during experiments at 200°C and at initial pressures higher than 2000 kPa.

Fig. 11 shows the width of the twilight-zone (i.e. the difference between the upper flammability limits obtained by the min–max and the tangent criterion) as function of the initial pressure ratio. Methane/air mixtures have a noticeable twilight-zone from 300 kPa initial pressure. This zone widens with increasing initial pressures. This appears not

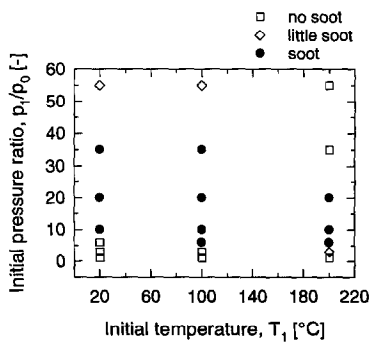

Fig. 10. Indication of the amount soot formation observed in an initial temperature–initial pressure diagram.

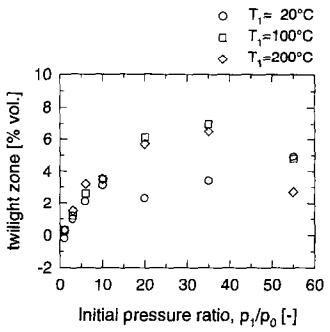

Fig. 11. The width of the twilight-zone as a function of the initial pressure ratio.

to be the case with increasing initial temperatures. It should be mentioned that the characteristics of the twilight-zone, which are small explosion pressures and temperatures, resemble the characteristics of the so called 'cool flame' zone [10]. However, this point was not clarified, and more investigation is needed.

4. Conclusions

Two different criteria to define a flammability limit have been used. It is found that the use of the tangent criterion could lead to a dangerous underestimation of the upper flammability limit, especially at high initial pressures.

Second order pressure dependence of the upper flammability limit is found instead of a logarithmic dependence as suggested by previous research. The temperature dependence of the UFL is found to be linear, which is in good agreement with previous research. However, the increase of the upper flammability limit is not a constant value of 8% [8] for a temperature increase of 100°C but depends on the initial pressure.

Near the upper flammability limit, two zones can sometimes be distinguished: a soot-zone and a twilight-zone. The presence of soot strongly depends on the initial conditions. The width of the twilight-zone increases with increasing initial pressures, but seems independent on the initial temperature.

It is to be recommended that more research is performed with other fuels to confirm the general validity of the pressure and temperature dependence of the UFL found in this study.

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