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Journal of Hazardous Materials A65 (1999) 233–244

**Journal of
Hazardous
Materials**

Pressure dependence of the auto-ignition temperature of methane/air mixtures

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Received 15 June 1998; revised 15 June 1998; accepted 4 January 1999

Abstract

The results of experiments conducted to determine the auto-ignition temperature (AIT) and the cool flame temperature (CFT) of methane/air mixtures at elevated pressures (200–4700 kPa) and for concentrations from 30 up to 83 vol.% are reported. The experiments were performed in a closed spherical vessel with a volume of 8 dm³. It is shown that methane/air mixtures can react spontaneously for methane concentrations far outside the flammability limits. Cool flames are observed for methane concentrations higher than 40 vol.%. The AIT and CFT are strongly pressure-dependent and decrease with increasing pressures. A Semenov correlation is developed for the CFT as a function of the pressure. The upper explosion limit (UEL) of methane/air mixtures at elevated pressure and temperature is linked with the CFT. It is shown that for certain conditions of pressure and temperature, the flammability range increases considerably even for a small temperature rise. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Safety; Auto-ignition; Explosion limits; Methane

1. Introduction

The ignitability of a flammable gas is characterised by its minimum ignition energy (MIE) and its auto-ignition temperature (AIT). The MIE is the lowest energy contents of a point ignition source which ignites the most ignitable mixture of a fuel and an oxidant.

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The AIT is defined as the lowest temperature to which a given mixture of a fuel and an oxidant must be heated to combust spontaneously in the absence of an ignition source. Neither the MIE nor the AIT of a given mixture are constants. They depend on the fuel concentration, flow condition, the initial pressure and volume of the mixture as well as the geometry of the explosion vessel. The present study is limited to the pressure dependence and the concentration dependence of the AIT.

In the past, the phenomenon of cool flames has been described. These flames emit a pale blue light [1] and are due to spontaneous reactions that occur at temperatures below the AIT. In these flames, the mixture reacts only partially. The process is accompanied by small pressure rises (i.e. pressure ratios smaller than two) and limited temperature rises (i.e. up to 150°C [1] or 200°C [2]). These effects may cause a mixture to enter the auto-ignition range [3]. The cool flame temperature (CFT) is defined as the lowest temperature at which a given mixture is capable of generating cool flames.

Several investigators [1,4,5] have shown that the lowest AITs of hydrocarbons occur at concentrations far outside the flammable range. However, the data that can be found in the literature on the AIT and CFT for combinations of increased pressure [6,7] and high fuel concentration [4,7] is very scarce.

In this study, the AIT and CFT are determined for methane/air mixtures at initial pressures from 200 kPa up to 4700 kPa and for concentrations ranging from 30 to 83 vol.%. First, the effect of the fuel concentration on the AIT and CFT is determined. Secondly, the effect of initial pressure on the AIT and CFT is determined for the most ignitable concentration. Thirdly, the effects of initial pressure and fuel concentration on induction time are studied. Finally, the results of this study are linked with previous measurements of the upper flammability limits of methane/air mixtures at elevated pressures and temperatures in the same apparatus [8]. Due to experimental limitations, the concentration dependence of the AIT, CFT and induction time was established only for one single temperature. As a consequence of the few experiments performed by Vliegen and Claessen [9], a temperature of 410°C was chosen.

2. Experimental apparatus and procedure

Fig. 1 illustrates the experimental apparatus. Basically, it consists of four parts:

1. a system that produces a homogeneous methane/air mixture at a desired concentration,
2. a buffer vessel of 8 dm³ which maintains the mixture at elevated pressure and at 150°C,
3. a 8 dm³ spherical explosion vessel which is evacuated and kept at the desired temperature and
4. a data acquisition system.

Mixtures of various concentrations were produced by means of two thermal mass flow controllers. A static mixing chamber ensures a homogeneous mixing of the two gas streams. Subsequently, the mixture flows into the evacuated preheated buffer vessel and is compressed to 10 000 kPa. The buffer vessel is connected to the explosion vessel by

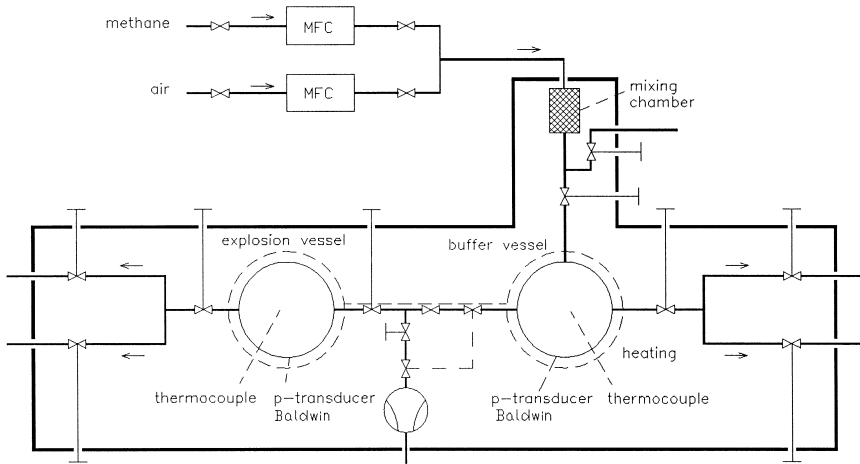


Fig. 1. Experimental apparatus.

means of a valved supply line, which is steam traced at 150°C. The evacuated explosion vessel is electrically heated to the desired temperature. The pressures in both vessels are measured with Baldwin 5000 PSI strain gauges while the temperature rises during the tests are measured with Cr/Al thermocouples placed in the centre of the vessel. For

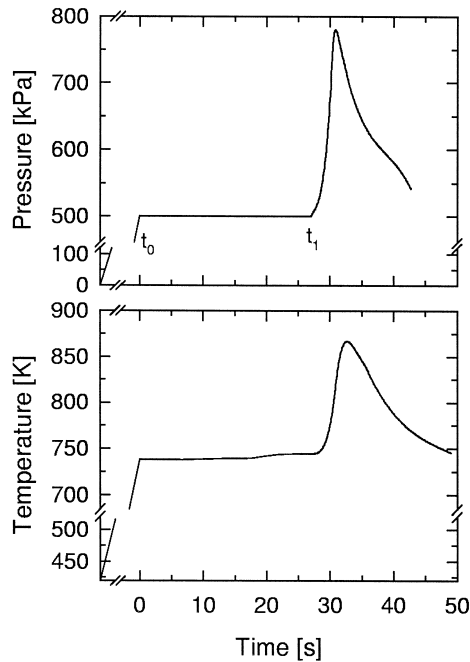


Fig. 2. Recorded pressure and temperature histories in the explosion vessel.

Table 1
Classification criteria

Type of reaction	Temperature rise	Maximum pressure ratio
No reaction	very small	= 1
Auto-ignition	> 200°C	> 1
Cool flame	< 200°C	< 2

each test series, a gas sample is taken from the buffer vessel and is analysed in a gas chromatograph (relative error 0.5%).

Fig. 2 shows typical pressure and temperature histories in the explosion vessel during a test. Before each test, the explosion vessel is evacuated and heated to the required temperature. Then, the gas mixture is introduced till the required pressure is reached (at time t_0). A sudden pressure rise occurs at t_1 , the start of the explosion. The induction time τ used in this study is defined as the difference between t_1 (start of the explosion) and t_0 (start of the test). These pressure and temperature measurements are necessary to consider whether the test was a cool flame or an auto-ignition. To get the AIT and CFT, the wall temperatures of the vessel were measured separately because the temperature of the mixture was different from the wall temperature.

Three types of scenarios can be observed (see Table 1). When no pressure or temperature increase is observed within 10 min, the attempt is considered unsuccessful and the test is considered not to give rise to an explosion. When both a pressure rise and a temperature rise larger than 200°C are recorded, auto-ignition has taken place. A temperature rise smaller than 200°C with a maximum pressure ratio of two or less is classified as a cool flame. The criterion to consider whether the test was an auto-ignition or a cool flame is chosen considering previous observations, namely small pressure rises and limited temperature rises. Due to practical problems, other characteristics of cool flames could not be recorded. Visual observations were impossible because of the high pressures and chemical analysis of the reaction products could not be performed.

3. Experimental results

3.1. Effect of fuel concentration on AIT and CFT

A first series of tests was aimed at identifying the mixture composition that ignites at the lowest initial pressure for a given mixture temperature. Different values are obtained depending upon the ignition criterion used: cool flame or auto-ignition.

Fig. 3 shows the maximum temperature rise (a) and the maximum pressure ratio (b) for various methane concentrations ignited at 410°C as a function of the initial pressure p_1 . Both the maximum temperature rise and the maximum pressure ratio increase with increasing initial pressure and decrease with increasing methane concentration.

From Fig. 3 a concentration-initial pressure ratio diagram with the cool flame and the auto-ignition region can be derived. This is shown in Fig. 4 in which p_1 is the initial

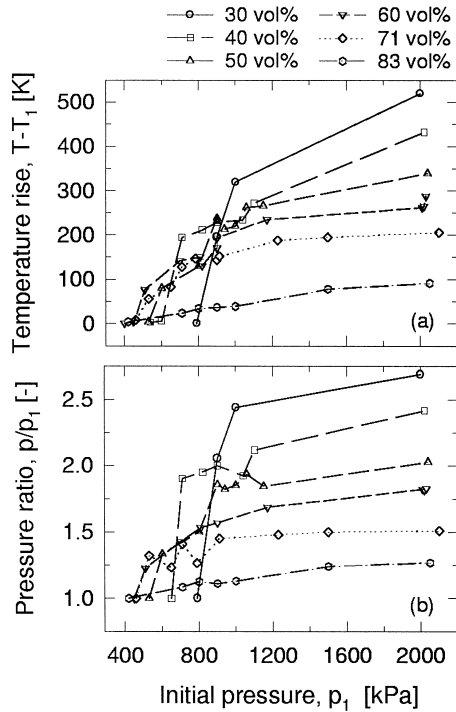


Fig. 3. Maximum temperature rise (a) and maximum pressure ratio (b) for various methane/air mixtures ignited at 410°C as a function of initial pressure.

pressure. The solid line represents the pressure limit beyond which auto-ignition occurs while the dashed line represents the pressure limit beyond which cool flames occur. No

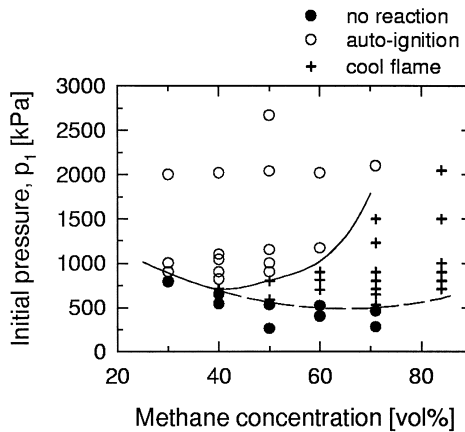


Fig. 4. Concentration–initial pressure diagram with the cool flame and the auto-ignition region, determined at 410°C.

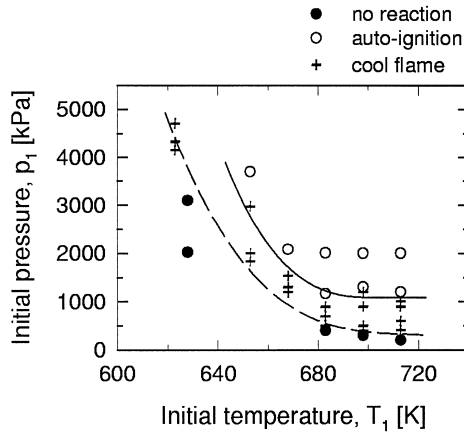


Fig. 5. Initial temperature–initial pressure diagram for the cool flame and the auto-ignition region, determined at 60 vol.% methane.

cool flames were observed for methane concentrations below 40 vol.%. The cool flame region begins at 40 vol.% and becomes wider with increasing methane concentrations.

From Fig. 4, the concentration showing the highest ignitability is found to be about 40 vol.% in terms of the AIT and about 60 vol.% in terms of the CFT. The corresponding initial pressures are 700 and 500 kPa, respectively. These concentrations are much higher than the 3 to 8 vol.% arrived at by Kong et al. [5] using a 1-l vessel at atmospheric pressure.

3.2. Effect of initial pressure on AIT and CFT

The pressure limits of the cool flame region and the auto-ignition region were determined for a methane concentration of 60 vol.% at a number of initial temperatures.

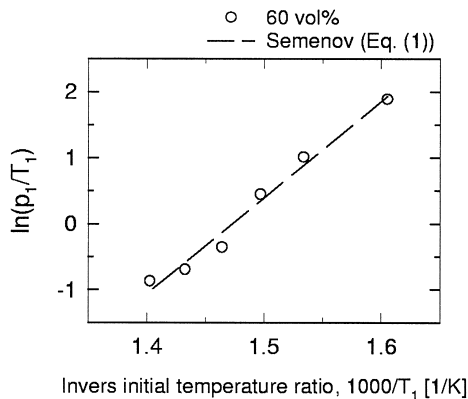


Fig. 6. The cool flame temperature correlated by a Semenov correlation.

Table 2
Value for the constants of Eqs. (1) and (2)

A_1	B_1	A_2	B_2
$14.54 \cdot 10^3$	-21.42	$13.88 \cdot 10^3$	-13.92

Fig. 5 shows the initial temperature-initial pressure diagram obtained. The solid line represents the pressures above which auto-ignition occurs while the dashed line represents the pressures above which cool flames occur. These boundary lines are determined by the method of least squares using the mean values of the measured points. Because of the large gaps between 'no reaction' and 'cool flame' points and between 'cool flame' and 'auto-ignition' points, the relative deviations of the boundary lines are between 10 and 15%. This explains why in some cases some data points are situated on the wrong side of the curve. Higher initial pressures lead to lower AITs and CFTs. This data clearly shows that the AIT and the CFT measured at atmospheric pressure should not be used at elevated initial pressures.

Due to the high inaccuracy, only the most dangerous temperature is correlated, namely the CFT. Fig. 6 shows the CFT in a $\ln(p_1/T_1) - 1/T_1$ diagram. Its linearity indicates that the CFT can be correlated by a relationship of the type proposed by Semenov [6,10]:

$$\ln\left(\frac{p_1}{T_1}\right) = \frac{A_1}{T_1} + B_1 \quad (1)$$

with p_1 the initial pressure (in kPa), T_1 the initial temperature or CFT (in K), and A_1 and B_1 constants determined by the method of least squares (Table 2). The relationship of Semenov is based on the thermal explosion model [6,10].

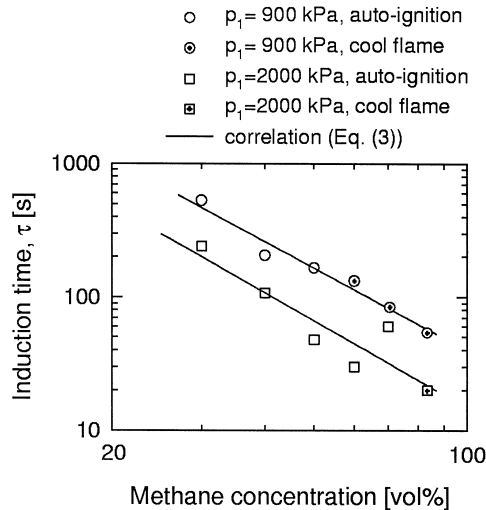


Fig. 7. Induction time vs. methane concentration for two initial pressures, determined at 410°C.

Table 3

Value for the constants of Eq. (3)

p_1 [kPa]	C_1 [s/vol.% ^{k_1}]	k_1 [–]
900	$501 \cdot 10^3$	–2.05
2000	$316 \cdot 10^3$	–2.16

In the literature [11,12], an empirical correlation between the CFT and the initial pressure which is much easier to use is often cited:

$$\ln(p_1) = \frac{A_2}{T_1} + B_2 \quad (2)$$

A_2 and B_2 , determined by the method of least squares, are listed in Table 2. Within the pressure range considered (i.e., 200 to 4700 kPa), the two correlations are equivalent.

3.3. Effect of methane concentration and initial pressure on the induction time

Fig. 7 shows the induction time as a function of methane concentration for two initial pressures (900 and 2000 kPa). The initial temperature equals 410°C. The vessel filling time was always much smaller than the induction time. Therefore, the influence of the vessel filling time on the AIT measurements can be neglected. The induction time strongly decreases with the increasing methane concentration. This observation confirms previous research [7,11]. The concentration dependence of the induction time can be correlated as follows:

$$\tau = C_1 [c]^{k_1} \quad (3)$$

with τ the induction time (in s), $[c]$ the methane concentration (in vol.%). C_1 and k_1 are constants, determined by the method of least squares which are listed in Table 3.

Fig. 8 shows the induction time as a function of initial pressure for two methane concentrations (60 and 83 vol.%). The initial temperature equals 410°C. The induction

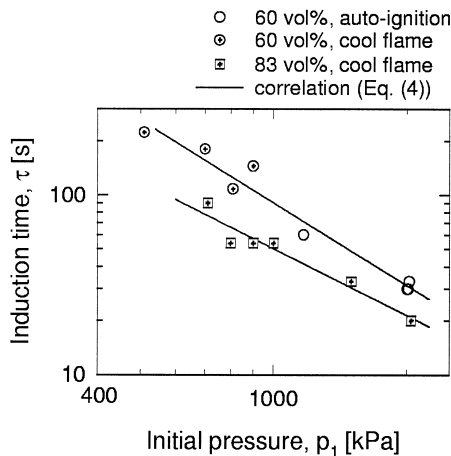


Fig. 8. Induction time vs. initial pressure for two methane concentrations, determined at 410°C.

Table 4
Value for the constants of Eq. (4)

[c] [vol.%]	C_2 [skPa k_2]	k_2 [–]
60	$3.77 \cdot 10^6$	1.54
83	$0.249 \cdot 10^6$	1.23

time strongly decreases with increasing initial pressure also. This observation confirms previous research [7,11]. In the auto-ignition region ($p_1 > 1000$ kPa at 60 vol.%), the induction times are smaller and less pressure-dependent than in the cool flame region. The pressure-dependence of the induction time can be correlated as follows [1]:

$$\tau = \frac{C_2}{p_1^{k_2}} \quad (4)$$

C_2 and k_2 are constants, determined by the method of least squares and listed in Table 4.

4. Auto-ignition and cool flame region as related to the flammability region

Vanderstraeten et al. [8] determined the upper flammability limit (UFL) of methane/air mixtures at pressures up to 5500 kPa and temperatures up to 200°C. These

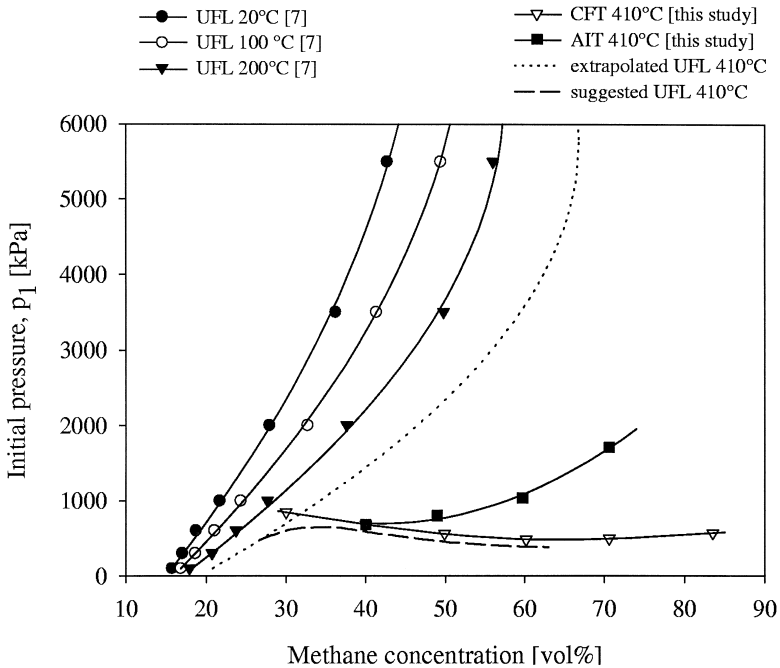


Fig. 9. Initial pressure vs. methane concentration for several initial temperatures.

Table 5
Coefficients of Eq. (5)

T_1 [°C]	UFL(p_0) [vol.%]	a [–]	b [–]
20	15.7	0.0466	–0.000269
100	16.8	0.0552	–0.000357
200	18.1	0.0683	–0.000541
410	20.8	0.0782	–0.000691

experiments were performed with the present apparatus provided with an ignition source. The results are shown in Fig. 9.

Vanderstraeten et al. correlated their data by means of one correlation for the pressure dependence of the UFL (Eq. (5)) and one correlation for the temperature dependence of the UFL (Eq. (6)):

$$\text{UFL}(p_1) = \text{UFL}(p_0) \left[1 + a \left(\frac{p_1}{p_0} - 1 \right) + b \left(\frac{p_1}{p_0} - 1 \right)^2 \right] \quad (5)$$

$$\text{UFL}(T_1) = \text{UFL}(T_0) \left[1 + c \left(\frac{T_1 - T_0}{100} \right) \right] \quad (6)$$

The resulting coefficients a , b and c are given in Tables 5 and 6. These correlations are only valid in the temperature range between 20° and 200°C. The UFLs at 410°C are derived with Eq. (6) for the different initial pressures. The coefficients a and b of correlation 5 drawn through the extrapolated UFLs are given in the last row of Table 5. The dotted line in Fig. 9 represents this extrapolated UFL at 410°C. Fig. 9 also contains the data of the present study for CFT and AIT at 410°C.

From the extrapolated UFL and the measured CFT as a function of the initial pressure, the real behaviour of the UFL at 410°C can be estimated. This is shown in Fig. 9 by means of the dashed line. It is found that from certain conditions (e.g. 410°C and 700 kPa), the UFL suddenly increases (from 30 to 90 vol.%).

Fig. 10 shows the same UFL and CFT data, but this time as a function of the initial temperature. The correlations for the temperature dependence of the UFL at 600 and 1000 kPa (Eq. (6)) are presented in Fig. 10 by means of dotted lines. The dashed lines

Table 6
Coefficients of Eq. (6)

p_1 / p_0 [–]	UFL(T_0) [vol.%]	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

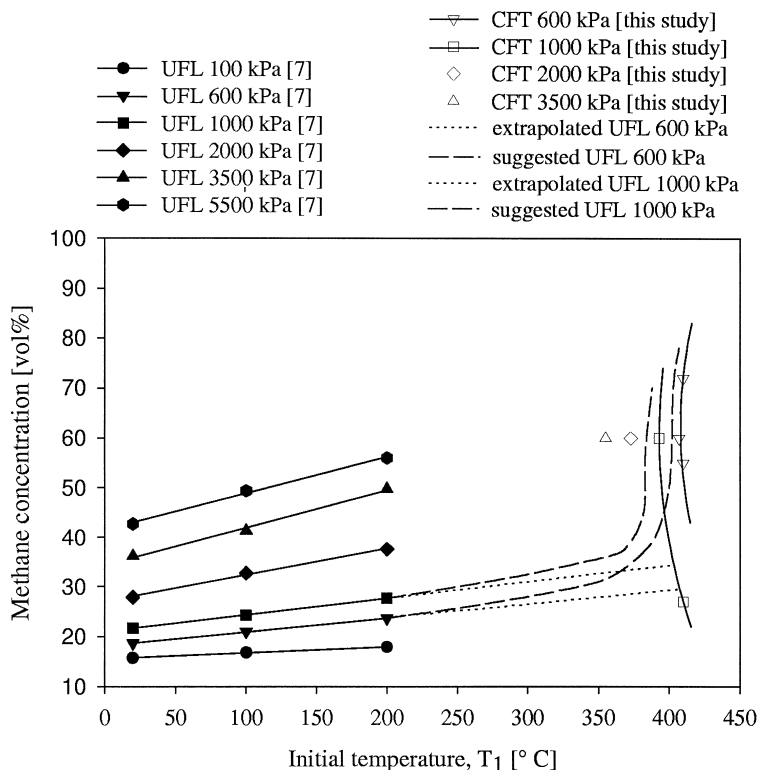


Fig. 10. Methane concentrations vs. initial temperature for several initial pressures.

correspond with the suggested behavior of the UFL as a function of initial temperature. This is nothing more than a suggestion. To know the real behavior of the UFL, it is necessary to perform more experiments.

5. Conclusions

Methane/air mixtures can react spontaneously even at concentrations much higher than the 'normal' upper flammability limit at the same temperature and pressure. Cool flames have been observed with methane concentrations higher than 40 vol.%.

The AIT and the CFT are strongly pressure-dependent and decrease with increasing pressure. At constant temperature, the induction time decreases with increasing methane concentration and increasing initial pressure.

The auto-ignition and cool flames regions can be represented in a three-dimensional diagram, as a function of pressure, concentration and temperature. In this study, only two planes of this diagram were examined, i.e. the pressure–temperature plane at 60 vol.% methane and the pressure–concentration plane at 410°C. To apply more widely the various trends that were observed in this study, further experiments are called for.

This study has been linked to a previous study about the influence of pressure and temperature on the upper flammability limit of methane/air mixtures. It is shown that, from certain initial conditions, the UFL suddenly increases. The lower the initial pressure, the higher the initial temperature should be before the UFL increases extremely. Additional experiments have to be done before the real behaviour of the upper flammability limit in the transition region is known. The authors have the intention to perform the necessary experiments in the future.

Acknowledgements

The authors are indebted to the Belgian Federal Ministry of Employment and Labour for providing support to perform this research project.

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