ARCHER

Collaborative Project (CP)

Co-funded by the European Commission under the Euratom Research and Training Programme on Nuclear Energy within the Seventh Framework Programme

Grant Agreement Number : 269892

Start date : 01/02/2011 Duration : 48 Months
www.archer-project.eu

Technical report on the flammability limits of air- Helium-H2-CH4- CO-CO2-H2O mixtures with dust

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ARCHER project – Contract Number: 269892
Advanced High-Temperature Reactors for Cogeneration of Heat and Electricity R&D
EC Scientific Officer: Dr. Panagiotis Manolatos

Document title	Explosive Gas Mixtures, Flammability Limits
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Number of pages	26
Document type	Deliverable
Work Package	WP2.2.1
Document number	Dsw.221 – revision 0
Issued by	CNRS-ICARE & IRSN
Date of completion	17/01./2014
Dissemination level	Restricted to the partners of the ARCHER project

Summary

This report presents the experimental work performed to define the flammability limits of He-H2-CO-CO2-H2O-CH4 mixtures which can be released to HTR containment during water ingress accident.
For this purpose, the methodology used aims assessing the flammability limits of H_2/CO/CH_4 based mixtures and the effect of the diluent on the flammability domain. The flammability domain for various conditions of initial pressures (1 and 5 bar), type of diluent (He or CO_2) and fuel concentrations has been measured in a stainless steel spherical bomb equipped with a high speed imaging system and a high frequency pressure transducer. The ignition was achieved using either a laser induced spark or an electric spark between two metallic electrodes. For each configuration, the energy provided to the mixture was measured. Four mixtures were identified by the partners as relevant to the safety analysis of these reactors: Two were constituted of H2 and CO, and for each mixture an equal amount of CH4 was added. These mixtures were labeled M1 to M4. For each mixture the minimum diluent content in order to suppress any combustion was determined, but also we have extended the study determine the whole flammability domain.

Approval

Rev.	Short description	First author	WP Leader	SP leader	Coordinator
0	First issue	N. Chaumeix (CNRS-ICARE) 27/10/2013		A. Bentaib	Name (org) ../../..

Distribution list

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All technical participants	ARCHER	
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1 Introduction

High temperature gas-cooled reactors are graphite moderated and helium cooled. The primary system consists of reactor pressure vessel, steam generator and hot gas duct vessel. The water ingress into the reactor pressure vessel can occur in case of the rupture of a heat transfer tube of the steam generator. The mixture of helium and steam will subsequently enter the reactor and will lead to a graphite corrosion of both fuel elements and graphite structures. This oxidation process can be responsible of the formation of He-H2-CO-CO2-H2O-CH4 mixtures.
The ingress of steam induces a pressure increase inside the reactor which may exceed the design pressure and leads to the opening of safety valves to the reactor hall.
Hence, a part of He-H2-CO-CO2-H2O-CH4 mixture could be released inside the reactor hall and may give birth to a flammable atmosphere. The determination, according to the initial temperature and pressure, of flammability limits of such explosive atmosphere needs to be addressed and is being investigated in the framework of ARCHER project.

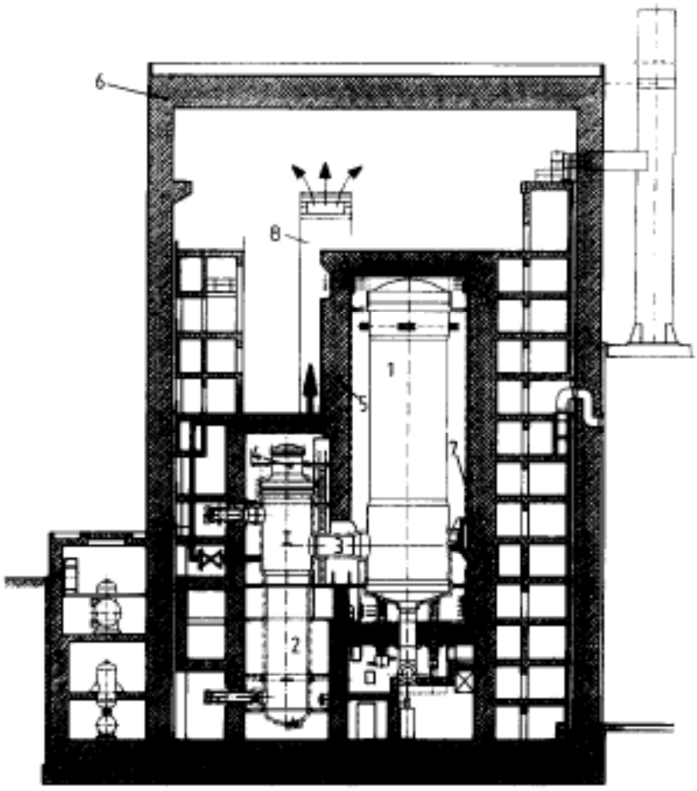


Figure 1: Vertical cross section of reactor building

For this purpose, experiments are performed on a dedicated device to assess the flammability limits of air-Helium-H2-CO-CO2-H2O-CH4 mixtures within different initial temperatures (25 up to 250°C) and at two different initial pressures (1 and 5 bars).

The definition of the corresponding matrix tests experiments had been performed based on the results available on the open literature dealing with water ingress scenarios in high temperature reactors.

2 Test matrix definition

Available literature related to water ingress scenarios in HTR shows that the most serious design basis scenario is postulated to be a double-ended guillotine break of a heating tube of the steam generator.
The discussion of such scenario had been given in [1] [2]. Following these references, both ends of the heating tube would initially release 6 kg/s of water and steam into the primary circuit.

The oxidation of hot graphite by steam had been investigated by several authors [3] [4]. The corresponding chemical reactions scheme is shown in the following table:

Réaction
$C(s) + H_2O(g) = CO(g) + H_2(g)$
$C(s) + 2H_2O(g) = CO2(g) + 2H_2(g)$
$CO(g) + H_2O(g) = CO_2(g) + H_2(g)$
$2CO(g) = C(s) + CO_2(g)$
$C(s) + 2H_2(g) = CH_4(g)$

Table 1: chemical reactions of graphite steam reaction

Consequently, water ingress could lead the formation of a mixture with the following gases: CO, CO_2, H_2, H_2O and CH_4. In the previous chemical reactions scheme, the two first reactions are preponderant. Hence, most of the available literature considers only these two reactions for the oxidation of graphite. Moreover, the considered oxidation rate r (kg/m^2/s) could be written as [4]:

$$r = \frac{k_A p_{H_2O}}{1 + k_B p_{H_2} + k_C p_{H_2O}}$$

Where P_{H2O} and P_{H2} stand for steam and hydrogen partial pressures. K_i are constant coefficients.

In case of water ingress scenarios, several safety systems are activated to limit the steam amount entering into the primary circuit. Nevertheless, the analysis of these scenarios given in [1] shows that:

- Case1 corresponds to a design basis scenario with safety actions. In this case, 600 kg of water and steam could enter into the primary circuit and react with the hot graphite leading to the production of 1000 kg of water gas (CO-H_2 mixtures). The atmosphere of the primary circuit will be constituted of 2700 kg of helium and 1000 kg of water gas.
- Case 2 corresponds to a severe accident situation assuming failure of the safety systems. The water quantity entering the primary circuit was evaluated to be 3300 kg by [1]. After completion of chemical reactions between steam and the hot graphite, the atmosphere of the primary circuit will be formed by 2700 kg of helium, 366 kg of hydrogen and 5130 kg of carbon monoxide.

As mentioned previously, water ingress is responsible of an increase of the primary circuit pressure leading to the opening of safety valves connecting this circuit to the reactor hall (see Fig1). Consequently, He-H_2-CO-CO_2-CH_4 mixture will be released to the reactor hall atmosphere which may become flammable. Reference 1 estimated also that with the safety valves operation, only 15% of this mixture will be released into the reactor hall.
Regarding severe accident situation and based on the previous indications, the following steps are adopted to define the flammability limits of these mixtures;

- Step 1: concerns the definition of 8 reference gas compositions with CO, H_2, CH_4. The composition of these reference gases will be done based on case 2 data.
- Step 2: He and CO_2 will be added to reference mixtures to investigate the effect of diluents on flammability limits.

2.1 Definition of gas reference composition

In case 2, the oxidation of graphite produces 366 kg of hydrogen and 5130 kg of carbon monoxide. To take into account the uncertainty of graphite oxidation modelling and to cover other situations, we consider two

values of hydrogen mass 200 kg and 600 kg and two values of carbon monoxide mass 4000 kg and 6000 kg. For methane, we consider two situations: (1) without methane and (2) with 200 kg of methane. The following table summarizes the obtained compositions:

Reference tests	Hydrogen mass (kg)	Carbon monoxide mass (kg)	Methane mass (kg)
Ref-1	**200**	**4000**	**0**
Ref-2	**200**	**6000**	**0**
Ref-3	**600**	**4000**	**0**
Ref-4	**600**	**6000**	**0**
Ref-5	**200**	**4000**	**200**
Ref-6	**200**	**6000**	**200**
Ref-7	**600**	**4000**	**200**
Ref-8	**600**	**6000**	**200**

Table 2: Reference tests.

The mean compositions of the fuel gas entering the reactor hall for each reference test (see table 2) are given in the following table:

Reference tests	H_2 molar fraction	CO molar fraction	CH_4 molar fraction
Ref-1	**0.4118**	**0.5882**	**0.0000**
Ref-2	**0.3182**	**0.6818**	**0.0000**
Ref-3	**0.6774**	**0.3226**	**0.0000**
Ref-4	**0.5833**	**0.4167**	**0.0000**
Ref-5	**0.3916**	**0.5594**	**0.0490**
Ref-6	**0.3060**	**0.6557**	**0.0383**
Ref-7	**0.6588**	**0.3137**	**0.0275**
Ref-8	**0.5695**	**0.4068**	**0.0237**

Table 3: Reference tests.

2.2 Experiments matrix tests

In the following, we assume that:

- Reactor hall volume = 5000 m^3,
- Reactor hall pressure =1 bar,
- Reactor hall temperature=27℃,
- 20% of gas mixture released from the primary circuit to the reactor hall.

To limit the number of experiments, flammability diagram will be determined for four mixtures selected from table 4. For each of the selected mixture, the minimum of CO_2, H_2O and He in order to inhibit the combustion will be determined for different equivalence ratios. These experiments will be performed at 2 different initial temperatures, 298 and 423 K(*).

Reference tests	H_2 molar fraction	CO molar fraction	CH_4 molar fraction
Ref-2	**0.3182**	**0.6818**	**0.0000**
Ref-3	**0.6774**	**0.3226**	**0.0000**
Ref-6	**0.3060**	**0.6557**	**0.0383**
Ref-7	**0.6588**	**0.3137**	**0.0275**

Table 4: Matrix tests

(*) further tests will be performed at higher temperature until 523K.

3 Experimental Setup

3.1 The Spherical Bomb

In the present work, ignitions of different mixtures were performed in a stainless steel spherical combustion chamber, or Spherical Bomb. Figure 2shows a schematic diagram of the experimental of the spherical bomb of the main windows and the different ports.

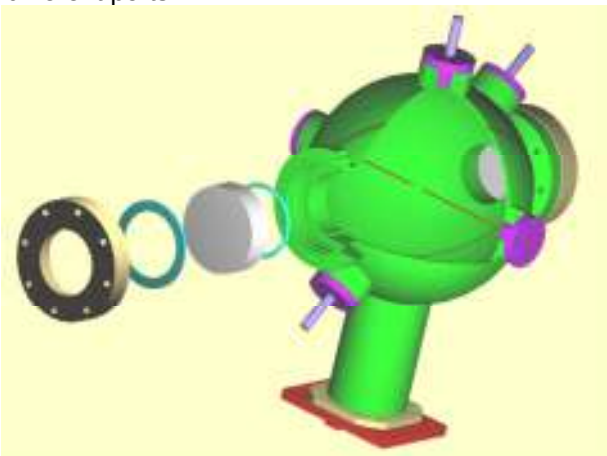


Figure 2 : Schematic of the Spherical Bomb of 250 mm diameter.

The spherical bomb, made of stainless steel, has an internal diameter of 250 mm and has 4 optical accesses (2 of 70 mm optical diameter and 2 of 20 mm optical diameter) made of quartz glass. It can sustain a pressure up to 50 bar. It has several ports that are used for several end-use:

i. To connect to the gas manifold ant to a primary vacuum pump. Before each run, the bomb is vacuumed to a pressure around 10 Pa before being filled with the studied mixture;
ii. To mount a temperature probe in order to measure the initial temperature of the wall before each run;
iii. To mount a pressure transducer that is used to monitor the pressure build-up inside the vessel due to the combustion;
iv. To mount the electrodes in case of an electric spark ignition,
v. To mount the windows in case of a laser induced ignition;

The ignition was initiated at the center of the vessel either by laser induced spark (LIS) or by electric spark discharge between two electrodes.

3.2 Diagnostics coupled to the spherical bomb

3.2.1 Flame Visualisation

The ignition and the subsequent flame propagation were visualized through a classical Z-type Schlieren setup with a high speed camera. The optical setup was the same as the one used by Lamoureux et al.[5] with slight modifications, a scheme of the optical layout is shown in Figure 3. It consists of two concave spherical mirrors (dia. 100 mm, focal length 0.5 m), and a light source was a DC 150 Watts Xenon lamp (Lot Oriel, Compact 150W Xe model). It was made as a point source via two lenses (dia. 75 and 20 mm and 150 and 22 mm focal lengths respectively).

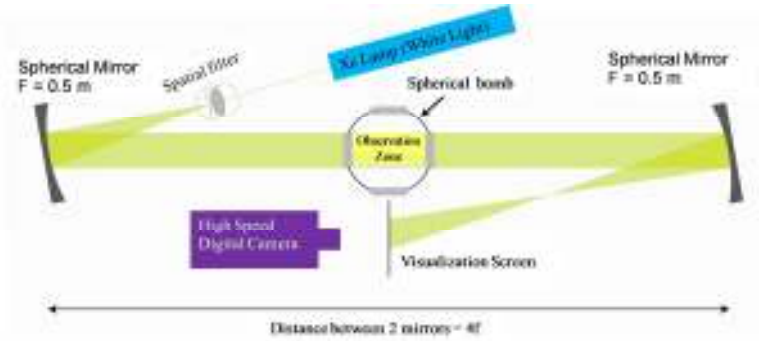
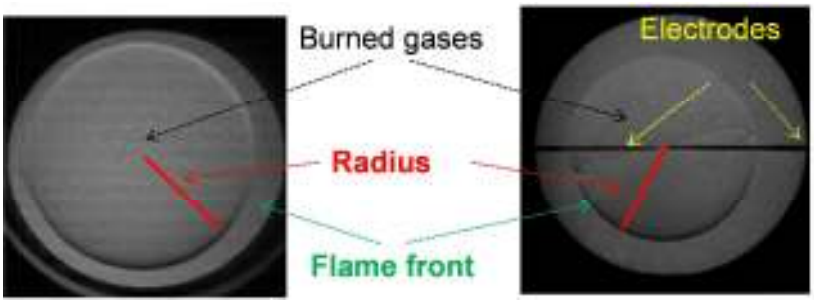


Figure 3 : Optical layout coupled with the spherical bomb.

Using the schlieren technique, it is then possible to visualize the density of the gradient and hence capture on a screen the location of the flame front as it is shown in Figure 4.



(a) (b)

Figure 4 : Snap shot of a flame during it's propagation in the bomb. (a) with laser spark induced ignition; (b) with electric spark ignition.

To perform this study, 2 different cameras were used during this study depending on the availability of the camera:

- Kodak, Ektapro HS4540 model. The maximum resolution of this camera is 256x256 pixels with a maximum speed of 4500 images/s.
- Photron, APX model, the maximum resolution of the camera is 564x564 at a framing rate of 4000 i/s.

The images are initially stored in the camera unit and then transferred to a PC before being processed.

Examples of images acquired during the tests are shown for different combustion regimes in .

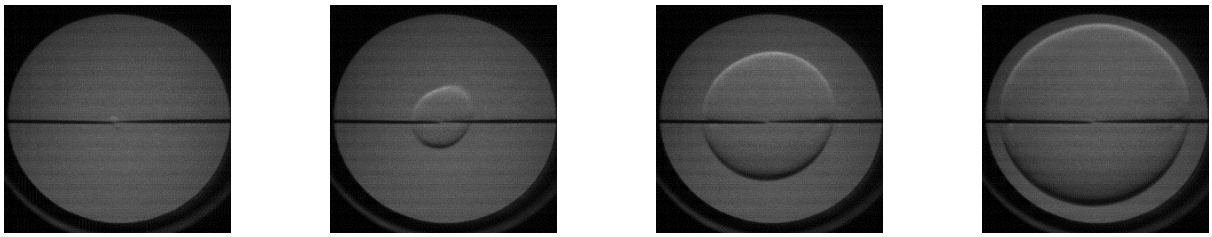


Image 2 Image 12 Image 22 Image 32

Run E2_012; Mixture: 0.7 {0.3166 H_2 + 0.6834 CO} + 0.30 Air.

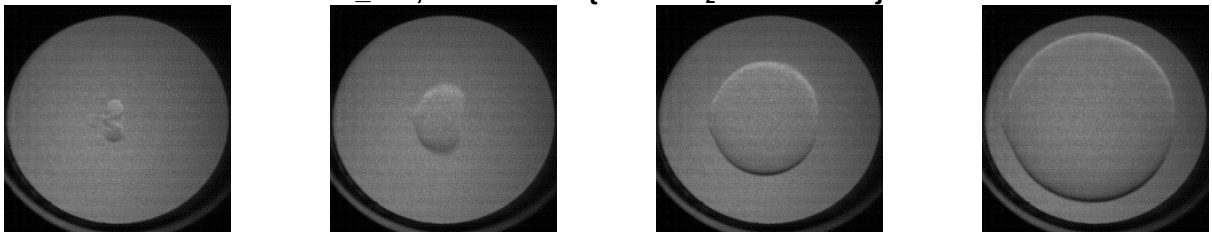


Image 1 Image 18 Image 35 Image 48

Run 126; Mixture : 0.41{0.6773 H_2+0.3227CO} + 0.338 Air + 0.2 CO_2

Figure 5 : Images acquired by the camera during the different tests of ignition. The initial temperature and pressure are 28℃ and 1 atm respectively.

3.2.2 Pressure measurements

During this work, two different types of pressures were measured: the over pressure due to the combustion when ignited and the partial pressures in order to prepare the mixture for the experiments. These 2 different type of measurements are performed using different pressure sensors.

The temporal behavior of the induced overpressure following the ignition was measured with a fast piezoelectric pressure transducer (Kistler 601A model). The overpressure signal was recorded on a digital oscilloscope (Tektronix, TDS2024B – 200 MHz). The sensitivity of the pressure transducer was chosen according to the initial pressure in the spherical bomb in order to minimize the error on the evaluation of the maximum pressure. An example of the recorded signal is given in Figure 6.

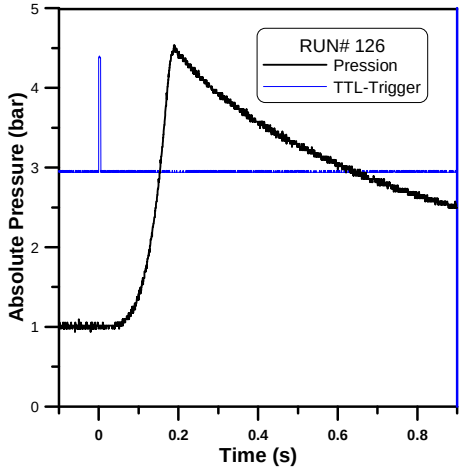


Figure 6 : Evolution of the Pressure signal in the spherical bomb in case of a successful ignition. The mixture is constituted of 0.41{0.6773 H_2+0.3227CO} + 0.338 Air + 0.2 CO_2. The initial temperature and pressure are 28℃ and 1 atm respectively.

For the mixture preparation, 2 different pressure transducers were used:

- For pressures lower than 1 atm, a capacitive pressure sensor (MKS 626-AX model) was used. The uncertainty on the reading is equal to 1.3 Pa.
- For pressures between 1 atm and 10 bar, a piezo-resistive pressure sensor was used (KISTLER, 5011) with a relative uncertainty estimated to be 4%.

3.3 Ignition System

3.3.1 Electrical Spark Ignition

In the case of ignition by electric spark, two thin horizontal tungsten electrodes, located along a diameter of the sphere, were used. Their diameter was about 1 mm. The distance between tips of the two electrodes was kept constant around roughly 2 mm. Indeed, as it has been shown by Lewis and von Elbe[6], the minimum ignition energy is usually obtained for electrode gaps around 2 mm. Moreover, in the case of free electrode tip (as in this study), the ignition is achievable even when the electrode gap is below the quenching distance. The 2 electrodes were linked to a high voltage power supply. The electric discharge was provided by an engine car ignition coil (Valeo, 245059 model) driven by an ignition module (Valeo, 245529). The energy storage time of the coil could be adapted between 400 µs and 2800 µs and for most of the experiments it was fixed to 1400 µs. A schematic of the ignition system coupled to the bomb is given in Figure 7.

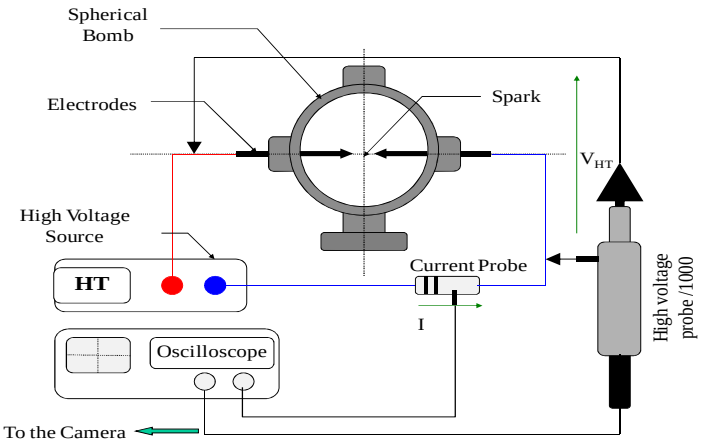


Figure 7 : Electric Spark ignition System coupled to the spherical bomb

The current I and voltage V of the electric discharge were measured with a current transformer (Bergoz, CT-D1.0) and a high voltage probe (Tektronix, P6015A), respectively, and acquired on a digital oscilloscope (Lecroy, WS434 – 350 MHz) as it can be seen on Figure 8.

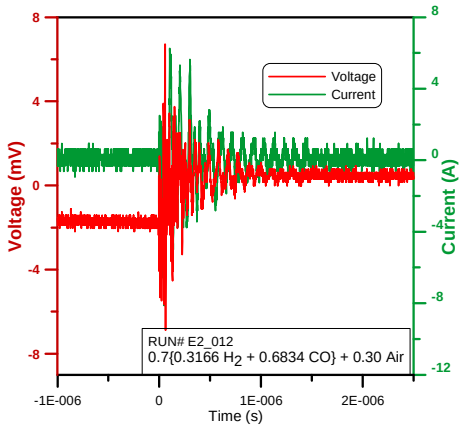
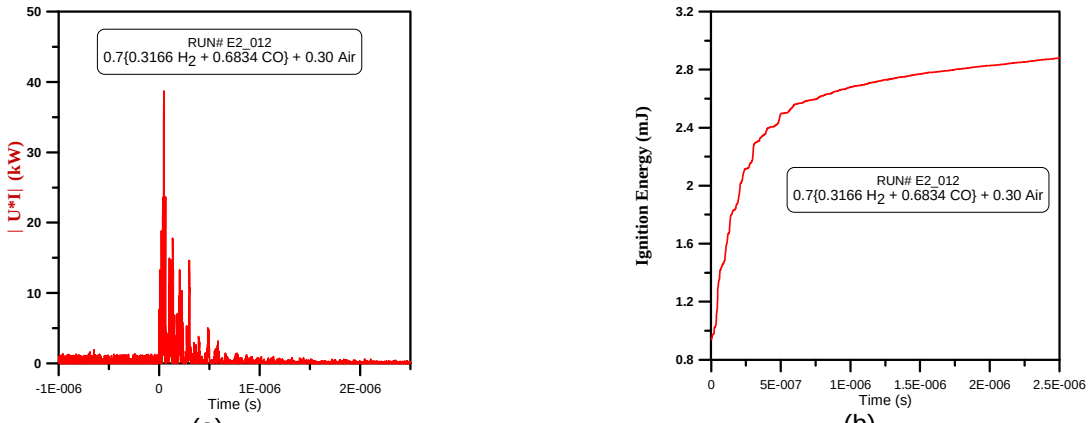


Figure 8 : Exemple of voltage and current measured at the eletrodes during the breakdown as a function of time. The mixture is constituted of 0.7 {0.3166 H_2 + 0.6834 CO} + 0.30 Air. The initial temperature and pressure are 28℃ and 1 atm respectively.

The amount of delivered electric energy is then deduced from the temporal integration of the product U*I as it is shown in Figure 9. In this example the energy is estimated to be 2.88 mJ.



(a) (b)

Figure 9 : Exemple of an evolution of the product U*I and of the Energy delivered by the electric spark as a function time. The mixture is constituted of 0.7 {0.3166 H_2 + 0.6834 CO} + 0.30 Air. The initial temperature and pressure are 28℃ and 1 atm respectively. The i gnition energy in this case is estimated to be 2.88 mJ.

3.3.2 Laser Induced Spark Ignition

In the case of LIS ignition, the laser used is a CILAS prototype Q-Switched DPSS Nd:YAG laser, working at 1064 nm and with a pulse duration about 13 ns. The laser head is 20 cm long and it consists in a folded cavity of approximately 1 meter long, providing a TEM00 laser beam, with a diameter of 3.2 mm and a M^2 = 1.6. The laser energy delivered per pulse can reach 80 mJ. A variable attenuator, consisting in the combination of a half wave-plate and a Glan-Taylor polarizer, is used to adjust with good accuracy and repeatability the laser energy delivered to achieve ignition of the mixture. In order to obtain sufficient energy densities at the focal point, before focusing, the beam diameter is expanded by a beam expander (Melles-Griot, HEB-4.0-10X) with a 10x magnification ratio. The beam is then reflected on a R_{max} mirror (of 50 mm diameter) and focused, through a quartz window of 20 mm diameter, at the center of the vessel with a f = 250 mm spherical lens. A schematic of the layout is presented in Figure 10.

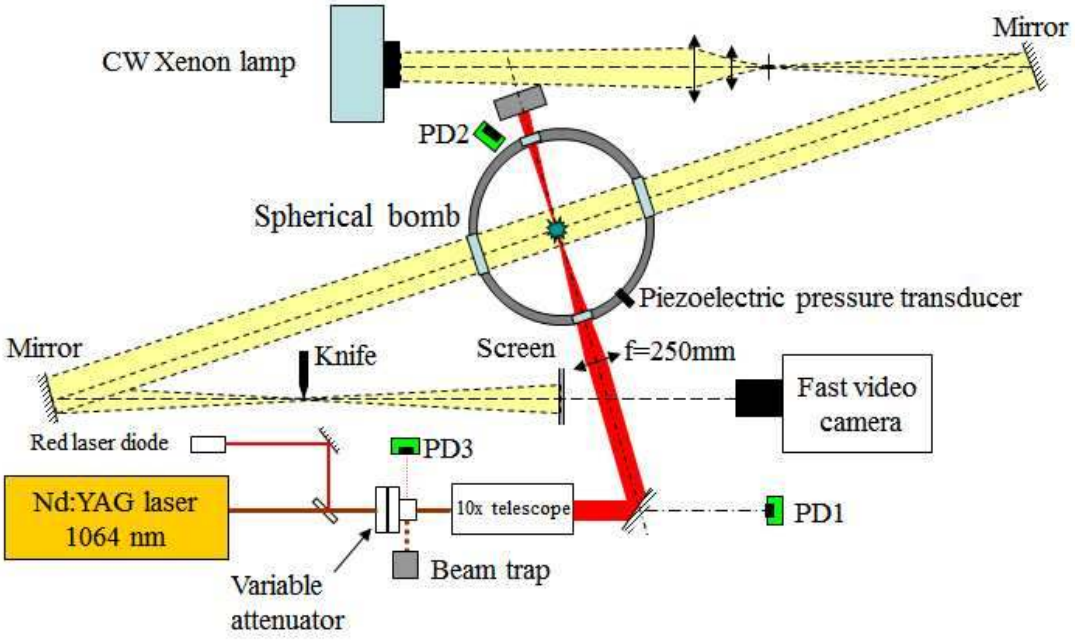


Figure 10 : Schematic of the experimental setup for the ignition of mixtures by LIS

A visible laser diode (635 nm) is used to help the alignment of all the optical components of the setup. All optical components have an AR coating at 1064 nm except the quartz windows. A first photodiode (PD1) (Thorlabs, DET10A) placed behind the R_{max} mirror is used to detect and measure a weak percentage of the energy delivered and transmitted by the laser beam inside the spherical bomb. A second identical photodiode 2 (PD2) detects part of the radiation diffused by the beam trap placed at the exit of the vessel and helps to detect the occurrence of the laser induced breakdown in the spherical bomb. The signals of PD1 and PD2 are transferred and recorded by the digital oscilloscope (Lecroy).

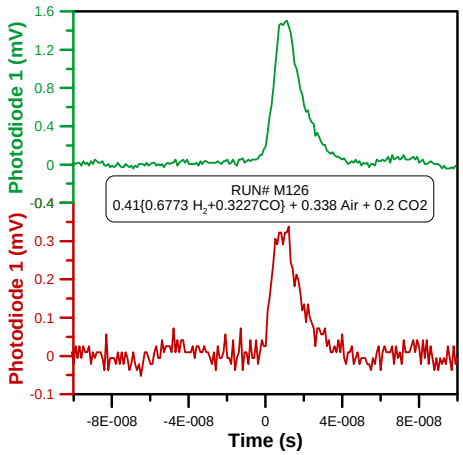


Figure 11 : Examples of recorded signals from the photodiodes 1 and 2. The mixture is constituted of 0.41{0.6773 H_2+0.3227CO} + 0.338 Air + 0.2 CO_2. The initial temperature and pressure are 28℃ and 1 atm respectively.

The amplitude of the delivered signal by the photodiode 1 is calibrated in energy through measurements with a laser joule-meter (Gentec, QE12SP). This calibration was made by increasing the transmitted laser energy through the attenuator. A neutral density filter with OD = 2.0 was mounted in front of the PD1 in order to avoid any saturation. Then, the calibration presented a perfect linearity.

As it will be further shown, the photodiode 2 does not permit to determine the transmitted energy during the laser breakdown. Nevertheless, we made a calibration with the spherical bomb under vacuum in order to avoid any laser breakdown and we obtained a good linearity of the sensitivity versus laser energy of the measured signal by PD2.
Taking into account the angular precision of the attenuator (± 0.5°), the SNR of the photodiode and st andard deviation of the calibration, the uncertainty on the laser pulse energy measurement was fixed to ±5%.

A digital delay generator (BNC, 575 model) is used to trigger the laser shot and the acquisition system of the camera. The photodiode 3, PhD3, (Thorlabs, DET10A) picks up a part of the beam diffused by the variable attenuator and is used to trigger the acquisitions on the two oscilloscopes.
In order to estimate with good accuracy the amount of laser energy delivered at the focal point, we measured a 12% global attenuation of the laser beam energy along its path, taking into account all the sources of attenuation, including vignetting of the beam entering the SB.

3.4 Mixtures Preparation

As mentioned in 2.2, the chosen reference combustible mixtures are:

- M1 : 0.6774 H_2 + 0.3226 CO which corresponds to Ref-3 mixture in Table 4,
- M2: 0.3182 H_2 + 0.6818 CO which corresponds to Ref-2 mixture in Table 4,
- M3 : 0.3060 H_2 + 0.6557 CO + 0.0383 CH_4 which corresponds to Ref-6 mixture in Table 4,
- M4 : 0.6588 H_2 + 0.3137 CO + 0.0275 CH_4 which corresponds to Ref-7 mixture in Table 4.

These mixtures were ordered from Air Liquide which provided the following composition of the CRYSTAL® grade mixtures:

- M1: {0.6773± 0.0063} H_2 + {0.3227± 0.0063} CO
- M2: {0.3166 ± 0.0063} H_2 + {0.6834 ± 0.0063} CO
- M3: {0.3056 ± 0.0061} H_2 + {0.03742 ± 0.00075} CH_4 + {0.65698 ± 0.00685} CO
- M4: {0.65825 ± 0.00684} H_2 + {0.3150 ± 0.0063} CO + {0.02675 ± 0.00054} CH_4

The air used was provided from our laboratory air compressor which is equipped with a dryer to remove any trace of humidity.

The combustible mixtures were diluted either by helium or carbon dioxide distributed by Air Liquide:

- Helium, grade U or alpha-gaz 1, has a purity better than 99.999 % with the following impurities: 3 ppm of H_2O, 2 ppm of O_2 and 0.5 ppm of Hydrocarbons;
- Carbon dioxide , grade N45, has a purity better than 99.995 % with the following impurities: 7 ppm of H_2O, 10 ppm of O_2, 2 ppm of CO, 1 ppm of H_2, 25 ppm of N_2 and 5 ppm of hydrocarbons.

The mixtures were prepared to achieve the desired equivalence ratio according to the partial-pressure method. Depending on the targeted partial pressure value, the MKS or the Kistler pressure transducer were used. The maximum relative uncertainty on the equivalence ratio ($\Delta\Phi/\Phi$) is between 0.2 and 0.8%.

4 Methodology

Flammability limits are defined as the lowest and highest fuel molar fractions for which a self-sustained flame is obtained at fixed initial temperature and pressure. A slight composition change in one direction produces a flammable mixture, in the other direction a non-flammable mixture. However, the experimental determination of limits of flammability is more difficult than may be expected because the flame propagation depends on several parameters such as the ignition source energy, location of the source, vessel geometry, and phenomena due to buoyancy and fresh gases movements. In the case of lean mixtures of hydrogen in air, flammability is especially sensitive to the location of ignition energy in the vessel and to the initial pressure of the mixture.

There have been several attempts to standardize the determination of flammability limits. Many data, often selected as references in literature, can be found in a report of Coward and Jones[7] who recommended a 2-in. glass tube which should be about 1.20-m long and ignited by a spark or by a small naked flame. In these tests the gas mixture was ignited and the eventual flame propagation was observed visually. To measure upward flame propagation, the gas mixture has to be ignited at the bottom and the flame may burn upward to the top of the tube. To measure downward flame propagation, the gas mixture is ignited at the top and the flame burns downward to the bottom. Two very different limit values corresponding to upward and downward propagation could be obtained for some mixtures. This was the case for the lean flammability limit of hydrogen in air (4.0 and 9.0 mol % H2 respectively). Bundesanstalt für Material-Prüfung Laboratory (B.A.M) used a closed spherical system of 20-cm diameter (5.34 L) with central spark ignition of high energy. The flammability limit criterion for a mixture at atmospheric pressure corresponds to an increase of 26 kPa in the chamber after ignition. In this case the lowest flammability limit was found to be equal to 3.9 mol% H_2[8].
Various old methods of determination are described for example by Médard[9]. The American Society for Testing and Materials has given standards for determining the flammability limits of chemicals at elevated temperature and pressure[10] and recommends a criterion corresponding to a pressure rise of at least 7% higher than the initial pressure for upward flame propagation when spark ignition is used as an ignition source in a closed vessel. The Pittsburgh Research Center (PRC) conducted all the gas flammability tests in a 120-L spherical vessel using standard tests procedures. Some of these tests have been applied to H_2/air mixture[11].

4.1 Flame Behavior

Far from the flammability limits, when the energy is provided, either by induced by a laser or by an electric spark, and is enough to induce a combustion, a spherical flame is formed in the center of the vessel and increases in size until it reaches the wall of the enclosure. With the visualization setup and the high speed camera, the images of the expanding flame are captured showing that the flame is spherical in shape (Figure 12).

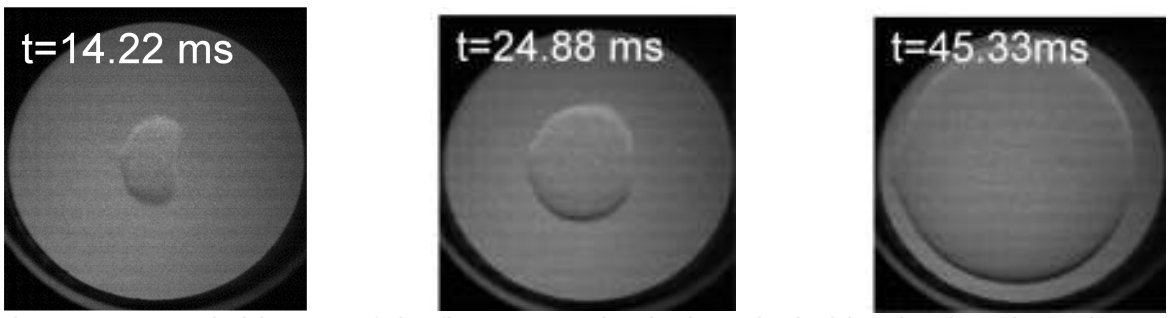


Figure 12: Recorded images of the flame expansion in the spherical bomb. The mixture is constituted of 41.2% {0.6774 H_2+0.3226 CO} + 33.8 % Air + 25% CO_2. The initial temperature and pressure are 28℃ and 1 atm respectively.

At the same time as the flame propagation recording, the pressure increase in the vessel due to the combustion is also measured and recorded on a digital scope. As it is shown in Figure 13, the pressure increases from the initial value of 1 bar and reaches a maximum of 4.50 bar which corresponds to the maximum pressure when all the available combustible mixture has burnt. The following decrease is due to the cooling of the burnt gases. The maximum pressure recorded by the pressure transducer can then be compared to the theoretical value calculated assuming an adiabatic combustion at constant volume, P_{AICC}.

The method will be presented in §4.2. For this mixture, the P_{AICC} was estimated to be 4.52 bar. The difference between the experimental maximum pressure and the theoretical is less than 0.5 %.

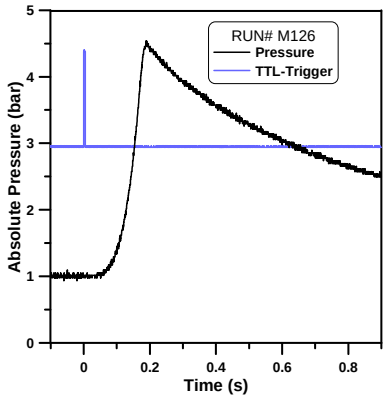


Figure 13: Pressure evolution as a function of time in the spherical bomb. The mixture is constituted of 41.2% {0.6774 H_2+0.3226 CO} + 33.8 % Air + 25% CO_2. The initial temperature and pressure are 28℃ and 1 atm respectively.

When a mixture with a composition close to the lower flammability limit is ignited, the flame obtained is not spherical anymore. As it is shown in Figure 14, the ignition leads to the formation a flame that propagates only in the upward direction. In this regime, the combustion wave will not propagate to the whole volume but only until it reaches the top wall were it will extinguish. Hence, the maximum pressure will be much lower than the theoretical one. For the example of Figure 14, the pressure recorded by the scope is given in Figure 15. As one can see, in this case the maximum pressure is 1.3 bar while the P_{AICC} is calculated to be 3.99 bar. The large difference is also an indicator of the incompleteness of the combustion.

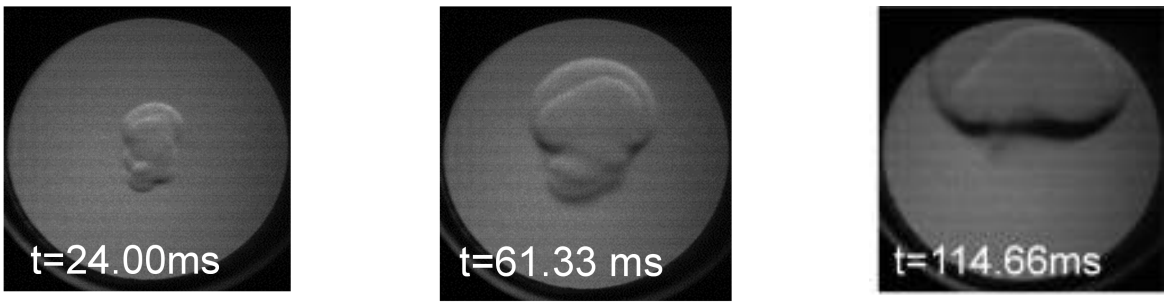


Figure 14: Recorded images of the flame expansion in the spherical bomb. The mixture is constituted of 12.6% {0.6774 H_2+0.3226 CO} + 37.5 % Air + 50% CO_2. The initial temperature and pressure are 28℃ and 1 atm respectively.

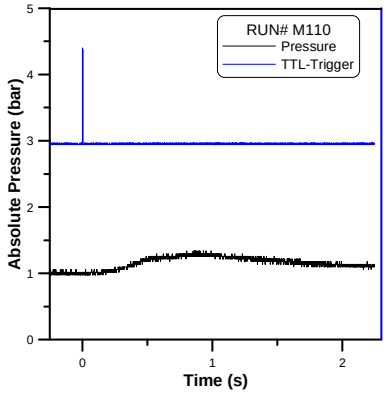


Figure 15: Pressure evolution as a function of time in the spherical bomb. The mixture is constituted of 12.6% {0.6774 H_2+0.3226 CO} + 37.5 % Air + 50%CO_2. The initial temperature and pressure are 28℃ and 1 atm respectively.

For mixtures corresponding to the flammability limit composition, the plasma induced by the laser is able to ignite locally the mixture, but this initial kernel fades away quickly and no sustainable flame is observed (Figure 16). The absence of combustion is also confirmed by the pressure recording inside the bomb. As it is shown in Figure 17, no variation in the pressure is recorded.

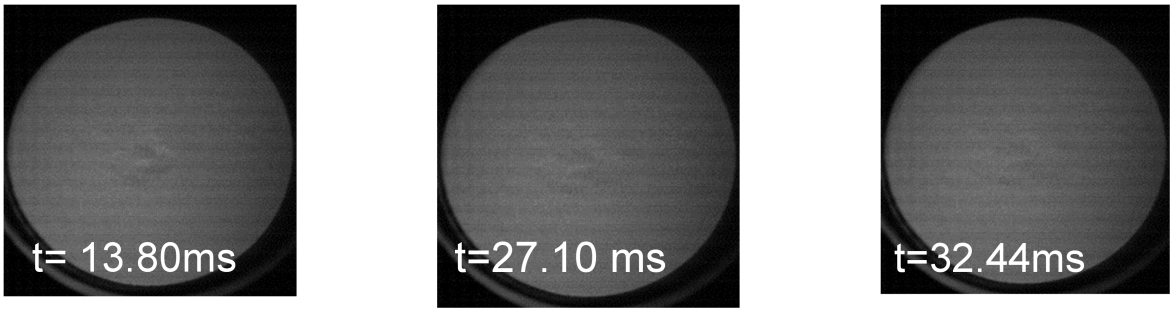


Figure 16: Recorded images of the failed igntion in the spherical bomb. The mixture is constituted of 6.79% {0.6774 H_2+0.3226 CO} + 60.2 % Air + 33% CO_2. The initial temperature and pressure are 28℃ and 1 atm respectively.

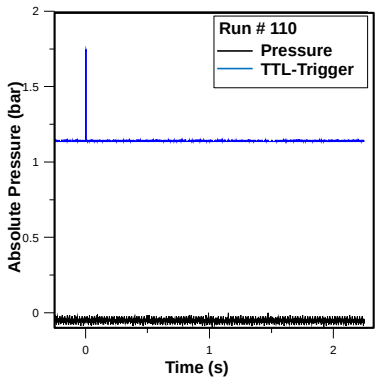


Figure 17: Pressure evolution as a function of time in the spherical bomb. The mixture is constituted of 6.79% {0.6774 H_2+0.3226 CO} + 60.2 % Air + 33% CO_2. The initial temperature and pressure are 28℃ and 1 atm respectively.

Hence, in this report the flammability limit will be defined as the minimum fuel molar fraction for which no combustion was observed after the local ignition occurred in the case of non-diluted mixtures. For the diluted mixtures, the flammability limit will be defined as the maximum diluent molar fraction that has to be added to the mixture in order to suppress the flame propagation.

4.2 Equilibrium calculations

The maximum pressure for an adiabatic combustion at constant volume, P_{AICC}, the flame temperature T_F and the expansion factor, σ, have been evaluated using the Equilibrium application of the code COSILAB[12].
These calculations are based on the knowledge of the thermodynamics properties of the reactants and of the products.

Since the mixtures studied are constituted of H2, CH4, CO diluted by either of the following diluents, He, CO_2 or H_2O_{vap}, the species, taken into account in the mechanism of the oxidation of methane[13], have been considered in the calculations:

- H2, H, O, O2, OH, H2O, HO2, H2O2,
- C, CH, CH2, CH2(S), CH3, CH4, CO, CO2, HCO, CH2O, CH2OH, CH3O, CH3OH, C2H, C2H2, C2H3, C2H4, C2H5, C2H6, HCCO, CH2CO, HCCOH, C3H7,C3H8, CH2CHO, CH3CHO
- N, NH, NH2, NH3, NNH, NO, NO2, N2O, HNO, CN, HCN, H2CN, HCNN, HCNO, HOCN, HNCO, NCO, N2, HE

5 Flammability Limits Results

5.1 Lower Flammability Limit

For each studied mixture, the minimum combustible mixture molar fraction in air, necessary to obtain a self-sustained flame, is determined.
The lower flammability limit is then determined when, for a given energy deposited in the medium, the local ignition is achieved and a flame kernel is created but:

- this kernel fades away very quickly and no combustion wave propagates;
- And no pressure rise is recorded inside the vessel.

The results for the lower flammability limit for the different mixtures at an initial pressure of 1 bar and at ambient temperature are summarized in Table 1.

Mixture Label	Mixture Composition	Lower Flammability Limit (molar %)
M1	0.6773 H_2 + 0.3227 CO	5.22 ± 0.03
M2	0.3166 H_2 + 0.6834 CO	8.01 ± 0.03
M3	0.3056 H_2 + 0.65698 CO+ 0.03742 CH_4	7.89 ± 0.03
M4	0.65825 H_2 + 0.3150 CO + 0.02675 CH_4	5.61 ± 0.02

Table 1: Lower Flammability Limit of the different mixtures initially at 1 bar and 26℃.

As one can see substituting 32.27 % of H_2 by CO leads to an increase of the lower flammability limit from 4 % to 5.2 % and when this substitution is increased to 68.34 % the lower flammability limit is raised again to 8 %. When methane is added, the effect is less noticeable. When part of the mixture M2 is substituted by methane, the lower flammability limit is only slightly change from 8.0 to 7.92 %; when part of M1 is substituted by methane the lower flammability limit varies also from 5.2 to 5.53 %.

A second series of experiments have been performed with an initial pressure of 5 bars at ambient temperature. The results are summarized in Table 2.

Mixture Label	Mixture Composition	Lower Flammability Limit (molar %)
M1	0.6773 H_2 + 0.3227 CO	6.57 ± 0.43
M3	0.3056 H_2 + 0.65698 CO+ 0.03742 CH_4	8.55 ± 0.43
M4	0.65825 H_2 + 0.3150 CO + 0.02675 CH_4	6.38 ± 0.43

Table 2: Lower Flammability Limit of the different mixtures initially at 5 bars and 26℃.

The LFL is slightly reduced when the pressure is increased from 1 to 5 bars. The strongest effect if observed for M1 which is the one with the highest content of H_2.

5.2 Upper Flammability Limit

The same methodology has been applied to determine the maximum molar fraction of the fuel mixture in air for which no sustainable flame was observed. In this case, when the ignition leads to the formation of a sustainable flame, the latter is spherical and a total combustion is observed. If the ignition does not lead to the formation of a flame, then no combustion wave is observed. There is no flame that would propagate only in the upward direction for rich conditions.

The results for the lower flammability limit for the different mixtures at an initial pressure of 1 bar and at ambient temperature are summarized in Table 3.

Mixture Label	Mixture Composition	Upper Flammability Limit (molar %)
M1	0.6773 H_2 + 0.3227 CO	70.61 ± 0.05
M2	0.3166 H_2 + 0.6834 CO	73.21 ± 0.05
M3	0.3056 H_2 + 0.65698 CO+ 0.03742 CH_4	57.90 ± 0.04
M4	0.65825 H_2 + 0.3150 CO + 0.02675 CH_4	58.49 ± 0.03

Table 3: Upper Flammability Limit of the different mixtures initially at 1 bar and 26℃.

In the case of the upper flammability limit, substituting H_2 by CO has a strong effect on this parameter. The upper flammability decreases from 75 % (for hydrogen in air) to 70.61 % for M1 and to 73.2 % for M2. Unlike for the lower flammability limit, methane has a very strong effect on the rich side since the lower flammability limit for M3 drops to 57.65 % (part of M2 is substituted by methane) and to 58.4 % in case of M4 (which corresponds of part of M1 substituted by methane).

From the second series experiments performed with an initial pressure of 5 bars, the upper flammability limit was inferred at ambient temperature. The results are summarized in Table 4.

Mixture Label	Mixture Composition	Upper Flammability Limit (molar %)
M1	0.6773 H_2 + 0.3227 CO	68.39 ± 0.67
M3	0.3056 H_2 + 0.65698 CO+ 0.03742 CH_4	57.06 ± 0.63
M4	0.65825 H_2 + 0.3150 CO + 0.02675 CH_4	58.37 ± 0.63

Table 4: Upper Flammability Limit of the different mixtures initially at 5 bar and 26℃.

The UFL is reduced when the initial pressure is increased from 1 to 5 bars and this effect is also more visible in the case of mixture M1 which has the highest content of H_2.

5.3 Inerting by Diluent

In this part, the aim is to determine the minimum molar fraction of diluent (CO_2, He or H_2O) that is needed in order to make the different combustible mixtures non-combustible. However, to have a better insight on the effect of the diluent on the flammability limit of different Fuel to Air Ratio, we have performed more detailed experiments which lead to a much larger campaign of experiments than what was planned initially in the program.

5.3.1 Carbon Dioxide Dilution

Several experiments have been performed in order to determine the minimum fraction of diluent that is needed in order to suppress any flame propagation in the mixture for different Fuel to Air ratios: 10/90, 15/85, 25/75, 35/65, 55/45.
In the case where no ignition was obtained, an average of 10 shots were performed, while when a flame was ignited with a propagation, either with a total or a partial combustion, the test was repeated 3 times.

The flammability limits obtained were then plotted in a ternary diagram where the combustible (red dots) and non-combustible mixtures (black dots) are reported (Figure 18) and the limit between these 2 regimes with a black dashed line.

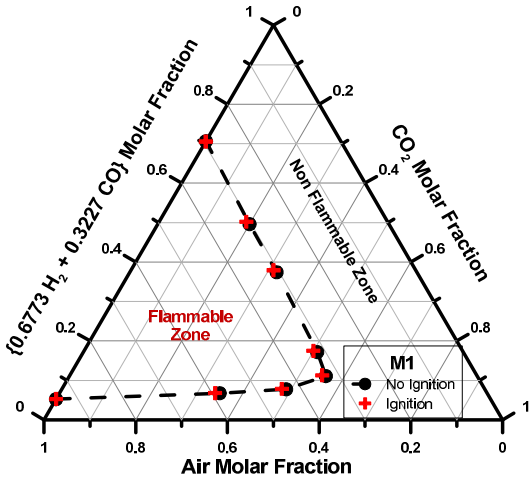


Figure 18: Ternary diagram reporting the flammability limits of the mixture M1 diluted by CO2. The initial temperature and pressure are 26℃ and 1 bar respectively.

Inside the limit, the mixture can be ignited and the combustion wave can either lead to a total flame propagation to the entire volume of the combustible mixture or lead to an upward flame propagation and subsequently to a partial combustion of the total volume.

The same diagrams have been determined experimentally for the 3 other mixtures and they are reported in Figure 19, Figure 20 and Figure 21.

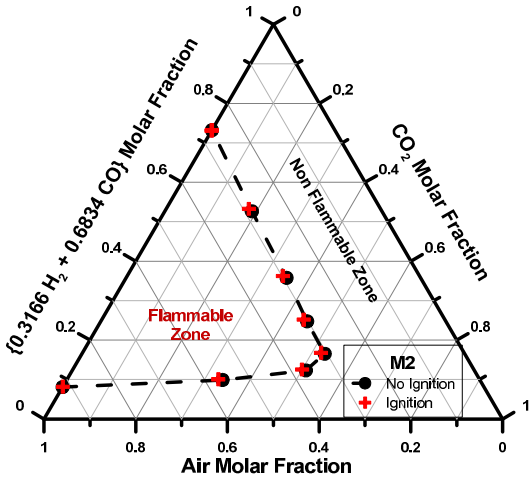


Figure 19: Ternary diagram reporting the flammability limits of the mixture M2 diluted by CO_2. The initial temperature and pressure are 26℃ and 1 bar respectively.

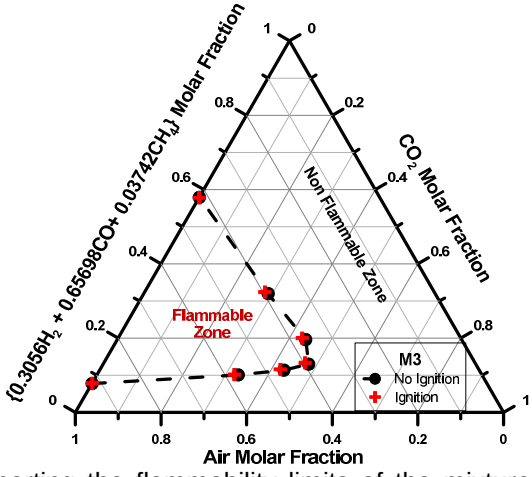


Figure 20: Ternary diagram reporting the flammability limits of the mixture M3 diluted by CO_2. The initial temperature and pressure are 26℃ and 1 bar respectively.

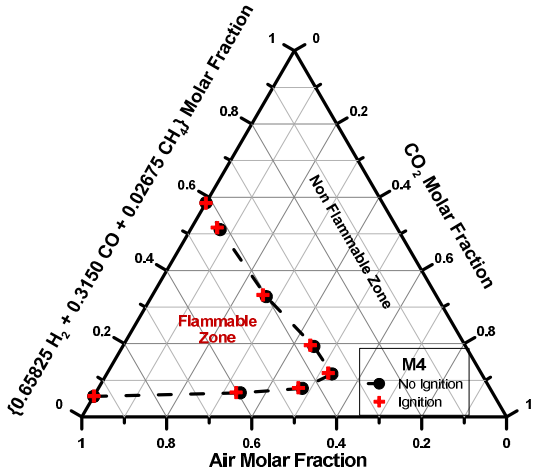


Figure 21: Ternary diagram reporting the flammability limits of the mixture M4 diluted by CO_2. The initial temperature and pressure are 26℃ and 1 bar respectively.

The minimum CO_2 molar fraction in order to inhibit totally any flame ignition and propagation is deduced from these experiments. This molar fraction is given, for each mixture, in Table 5

Mixture Label	Fuel Mixture Composition before dilution	CO_2 content in the mixture (molar %)
M1	0.6773 H_2 + 0.3227 CO	55.92 ± 0.04
M2	0.3166 H_2 + 0.6834 CO	52.93 ± 0.04
M3	0.3056 H_2 + 0.65698 CO+ 0.03742 CH_4	47.99 ± 0.04
M4	0.65825 H_2 + 0.3150 CO + 0.02675 CH_4	53.00 ± 0.03

Table 5: Minimum Carbon dioxide molar percent in order to suppress any combustion. The different mixtures were initially at 1 bar and 26℃.

By comparing the minimum amount of CO_2 in order to suppress any combustion of the different mixtures, one can see that:

- When hydrogen is substituted by carbon monoxide, M1 and M2, the highest CO_2 concentration needed to inhibit the flame ignition and propagation correspond to the mixture with the highest content of H_2 as it is shown in Figure 22. The combustible domain of M2+CO_2 is shifted toward higher concentration of fuel
- When part of the binary mixture is substituted by methane, by comparing M1 and M4 on one hand (Figure 23) and M2 and M3 on the other hand (Figure 24), less carbon dioxide is needed to suppress the combustion in the mixture. For both mixtures, the flammability limit on the lean side is almost not affected by the methane addition. On the contrary of the rich branch where the presence of methane reduces strongly the flammability domain.

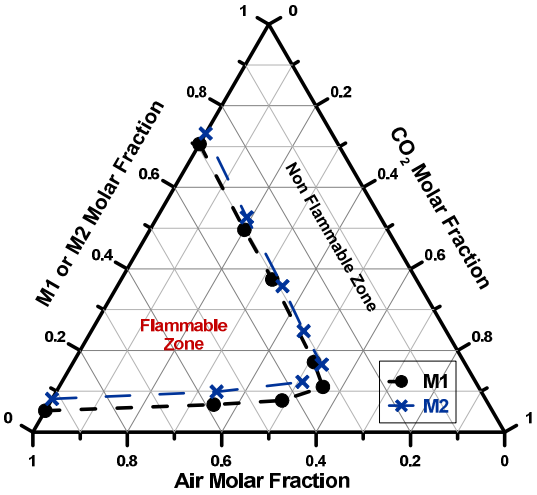


Figure 22: Effect of the H2/CO ratio on the flammability limit with CO_2. Comparison between M1 and M2 ternary diagram. The initial temperature and pressure are 26℃ and 1 bar respectively.

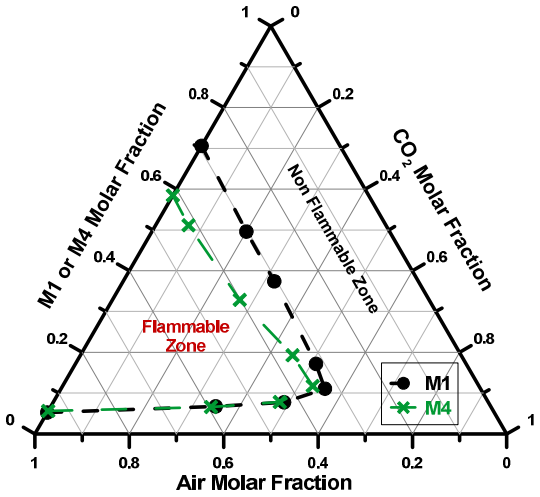


Figure 23: Effect of the methane addition on the flammability limit with CO_2. Comparison between M1 and M4 ternary diagram. The initial temperature and pressure are 26℃ and 1 bar respectively.

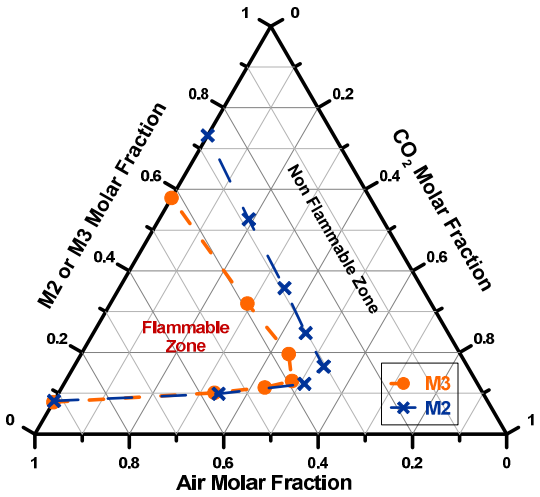


Figure 24: Effect of the methane addition on the flammability limit with CO_2. Comparison between M2 and M3 ternary diagram. The initial temperature and pressure are 26℃ and 1 bar respectively.

5.3.1 Helium Dilution

As in the case of Helium dilution, several experiments have been performed in order to determine the minimum fraction of He that is needed in order to suppress any flame propagation in the mixture for different Fuel to Air ratios: 10/90, 15/85, 25/75, 35/65, 55/45.
In the case where no ignition was obtained, an average of 10 shots were performed, while when a flame was ignited with a propagation, either with a total or a partial combustion, the test was repeated 3 times.

Following the same presentation as the CO_2 dilution results, the measured flammability limits were then plotted in a ternary diagram where the combustible (red dots) and non-combustible mixtures (black dots) are reported (Figure 25 to Figure 28) and the limit between these 2 regimes with a black dashed line.

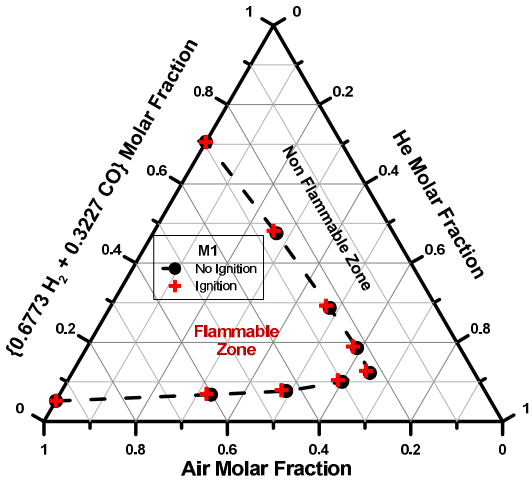


Figure 25: Ternary diagram reporting the flammability limits of the mixture M1 diluted by He. The initial temperature and pressure are 26℃ and 1 bar respectively.

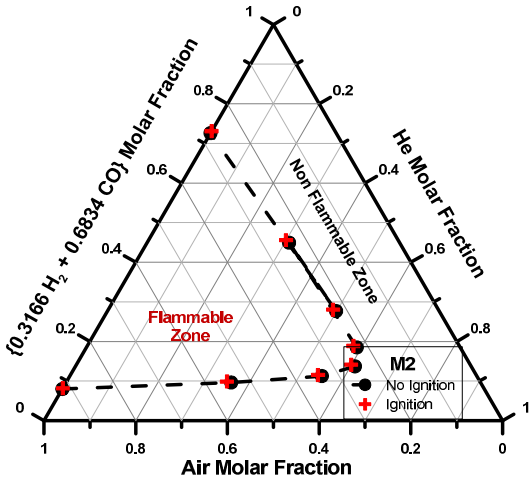


Figure 26: Ternary diagram reporting the flammability limits of the mixture M2 diluted by He. The initial temperature and pressure are 26℃ and 1 bar respectively.

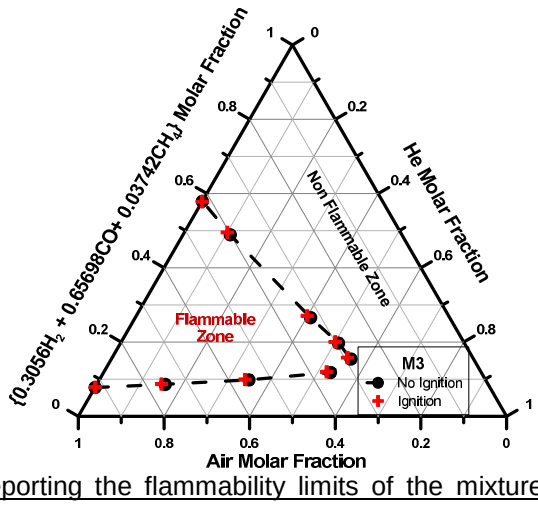


Figure 27: Ternary diagram reporting the flammability limits of the mixture M3 diluted by He. The initial temperature and pressure are 26℃ and 1 bar respectively.

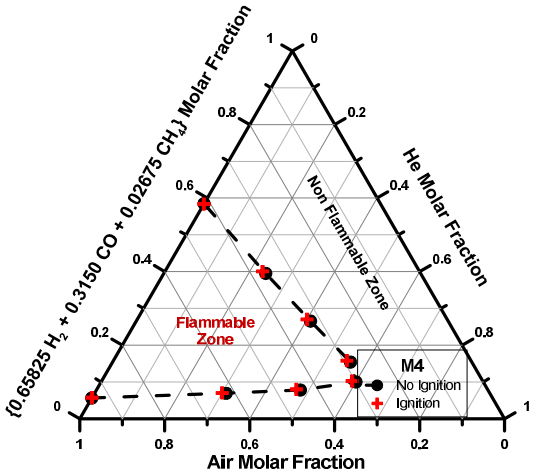


Figure 28: Ternary diagram reporting the flammability limits of the mixture M4 diluted by He. The initial temperature and pressure are 26℃ and 1 bar respectively.

The minimum He molar fraction in order to inhibit totally any flame ignition and propagation is deduced from these experiments. This molar fraction is given, for each mixture, in Table 6.

Mixture Label	Fuel Mixture Composition before dilution	He content in the mixture (molar %)
M1	0.6773 H_2 + 0.3227 CO	64.92 ± 0.04
M2	0.3166 H_2 + 0.6834 CO	60.94 ± 0.04
M3	0.3056 H_2 + 0.65698 CO+ 0.03742 CH_4	55.93 ± 0.04
M4	0.65825 H_2 + 0.3150 CO + 0.02675 CH_4	60.00 ± 0.03

Table 6: Minimum Helium molar percent in order to suppress any combustion. The different mixtures were initially at 1 bar and 26℃.

The same conclusions as the ones made for the dilution with CO_2 can be made in the case of He:

- The domain of flammability is shifted towards higher molar fraction of fuel
- The minimum He content in order to inert completely the mixture is lower when the H_2/CO ratio is lower

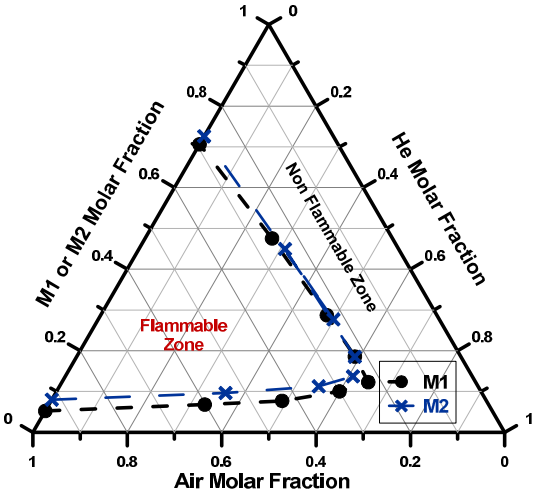


Figure 29: Effect of the H_2/CO ratio on the flammability limit with He. Comparison between M1 and M2 ternary diagram. The initial temperature and pressure are 26℃ and 1 bar respectively.

As when CH_4 is added to the mixture, similar conclusions as the ones for the flammability limits with CO_2 as a diluent, can also be drawn for the flammability limits with He:

- The presence of methane, for mixtures on the lean branch, has no noticeable effect on the flammability limit as it can be seen Figure 30 and Figure 31;
- However it reduces drastically the flammability domain on the rich branch side;
- The minimum amount of helium to supress totally the combustion is reduced for mixtures with methane.

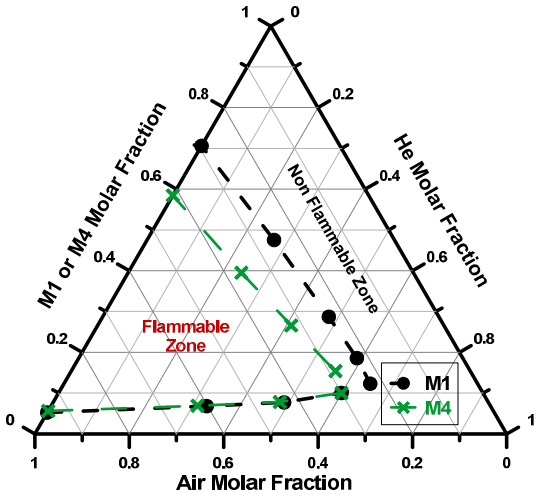


Figure 30: Effect of the methane addition on the flammability limit with He. Comparison between M1 and M4 ternary diagram. The initial temperature and pressure are 26℃ and 1 bar respectively.

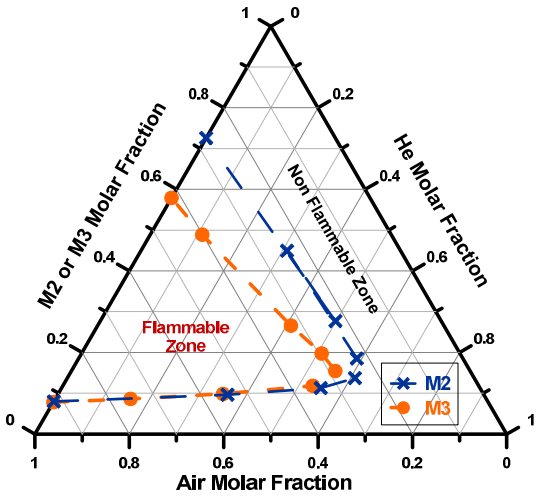


Figure 31: Effect of the methane addition on the flammability limit with He. Comparison between M2 and M3 ternary diagram. The initial temperature and pressure are 26℃ and 1 bar respectively.

5.4 Initial Pressure Effect on ternary diagrams

The ternary diagrams for mixtures M1, M3 and M4 have been determined at an initial pressure of 5 bars and at an initial temperature around 26℃. The same methodology as the one described for the experiments at 1 bar has been used. For these experiments, in the case where no ignition was obtained, an average of 10 shots were performed, while when a flame was ignited with a propagation, either with a total or a partial combustion, the test was repeated 3 times.

Several experiments have been performed in order to determine the minimum fraction of diluent that is needed in order to suppress any flame propagation in the mixture for different Fuel to Air ratios: 10/90, 15/85, 25/75, 35/65, 55/45.

The flammability limits are plotted as a ternary diagram for the 3 studied mixtures in the following figures. To illustrate the effect of the pressure on the flammability limits, the limits for an initial pressure of 1 bar are also reported.

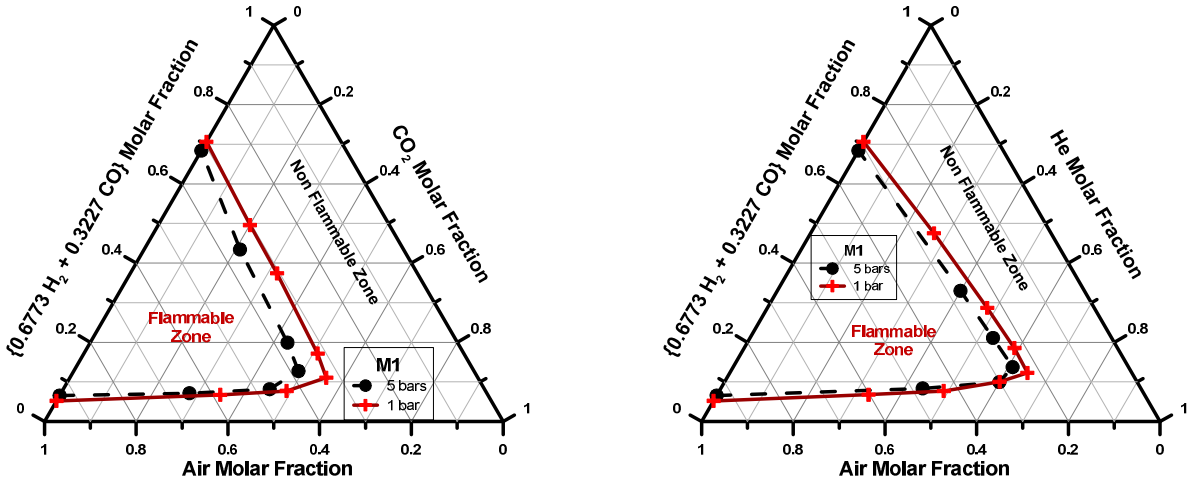


Figure 32: Effect of the initial pressure on the flammability diagram of the mixture M1 diluted by (a) CO_2 and (b) He. The initial temperature is around 26℃. Bla ck solid circle : 5 bars, red solid cross: 1 bar.

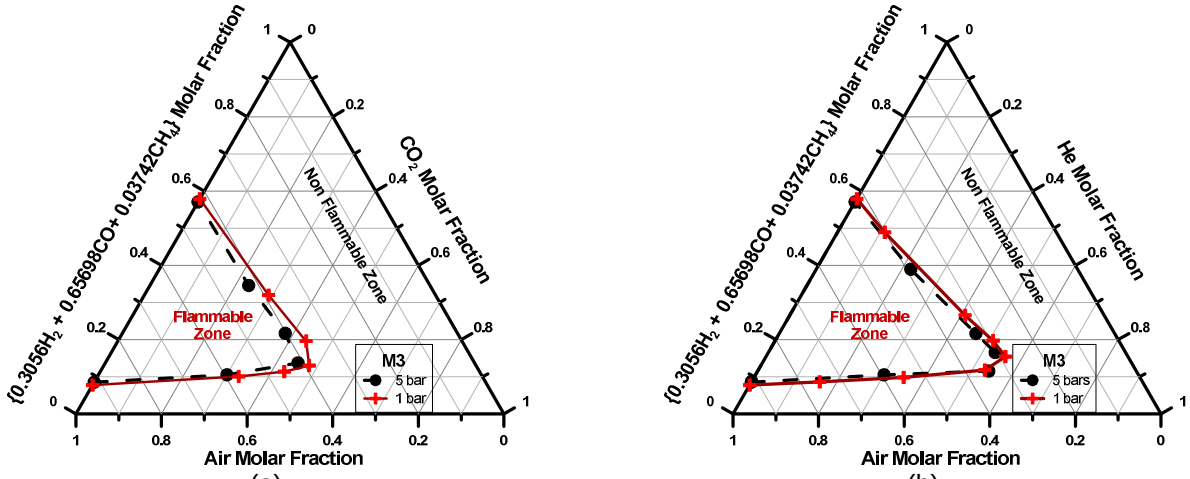


Figure 33: Effect of the initial pressure on the flammability diagram of the mixture M3 diluted by (a) CO_2 and (b) He. The initial temperature is around 26℃. Bla ck solid circle : 5 bars, red solid cross: 1 bar.

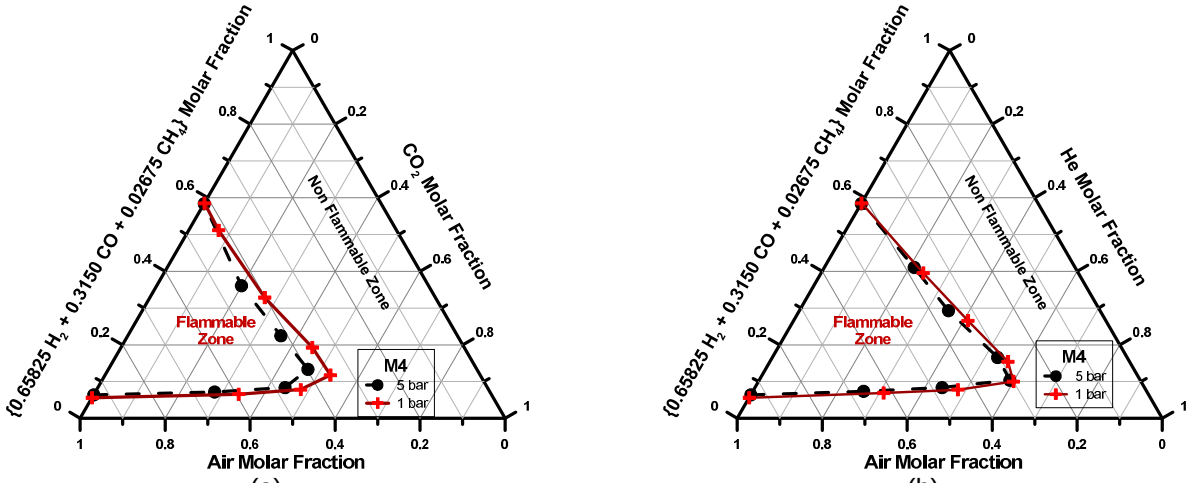


Figure 34: Effect of the initial pressure on the flammability diagram of the mixture M4 diluted by (a) CO_2 and (b) He. The initial temperature is around 26℃. Bla ck solid circle : 5 bars, red solid cross: 1 bar.

For all the 3 studied mixtures, the effect of adding the diluent on the lower branch of the diagram has almost no effect on the flammability limits at an initial pressure of 5 bars as it was observed at an initial pressure of 1 bar. Moreover, the lower branch of the flammability limit is only marginally reduced by the increase of the initial pressure.

For the upper branch of the flammability limit, the effect of both the initial pressure and the dilution is more pronounced:

- increasing the initial pressure for the same amount of diluent leads to a decrease of the flammability domain;
- increasing the diluent content leads also to a reduction in the flammability domain.

The minimum CO_2 molar fraction in order to inhibit totally any flame ignition and propagation is deduced from these experiments. This molar fraction is given, for each mixture, in Table 7.

Mixture Label	Fuel Mixture Composition before dilution	CO_2 content in the mixture (molar %)
M1	0.6773 H_2 + 0.3227 CO	49.00 ± 0.60
M3	0.3056 H_2 + 0.65698 CO+ 0.03742 CH_4	45.02 ± 0.58
M4	0.65825 H_2 + 0.3150 CO + 0.02675 CH_4	46.92 ± 0.59

Table 7: Minimum Carbon dioxide molar percent in order to suppress any combustion. The different mixtures were initially at 5 bar and 26℃.

The minimum He molar fraction in order to inhibit totally any flame ignition and propagation is deduced from these experiments. This molar fraction is given, for each mixture, in Table 8.

Mixture Label	Fuel Mixture Composition before dilution	He content in the mixture (molar %)
M1	0.6773 H_2 + 0.3227 CO	60.96 ± 0.64
M3	0.3056 H_2 + 0.65698 CO+ 0.03742 CH_4	53.98 ± 0.62
M4	0.65825 H_2 + 0.3150 CO + 0.02675 CH_4	58.96 ± 0.64

Table 8: Minimum Helium molar percent in order to suppress any combustion. The different mixtures were initially at 5 bars and 26℃.

For the 3 mixtures studied at an initial pressure of 5 bars, the domain for which a self-sustainable flame is obtained is included within the flammability domain determined at 1 bar.

6 Conclusion

This report is a summary of the experimental work that has been carried out at the laboratory ICARE of the CNRS in Orléans, France. The initial objective of the work was to measure the maximum diluent necessary to suppress any ignition of mixtures relevant to the safety of advanced high-temperature reactors. The analysis, by the partners of the project, of the different scenarios leading to a release of combustible gases led to the identifications of four combustible mixtures constituted with H_2, CO and CH_4. The aim was then to measure the maximum concentration of CO_2 or He to suppress any combustion. Within the framework of this project we have extended our measurements to the determination of the total domain flammability.
The flammability domain for each mixture (labeled from M1 to M4) has been determined using either CO_2 or He at an initial pressures of 1 and 5 bars. The following figure illustrates the flammability domain measured within this work for all the studied conditions.

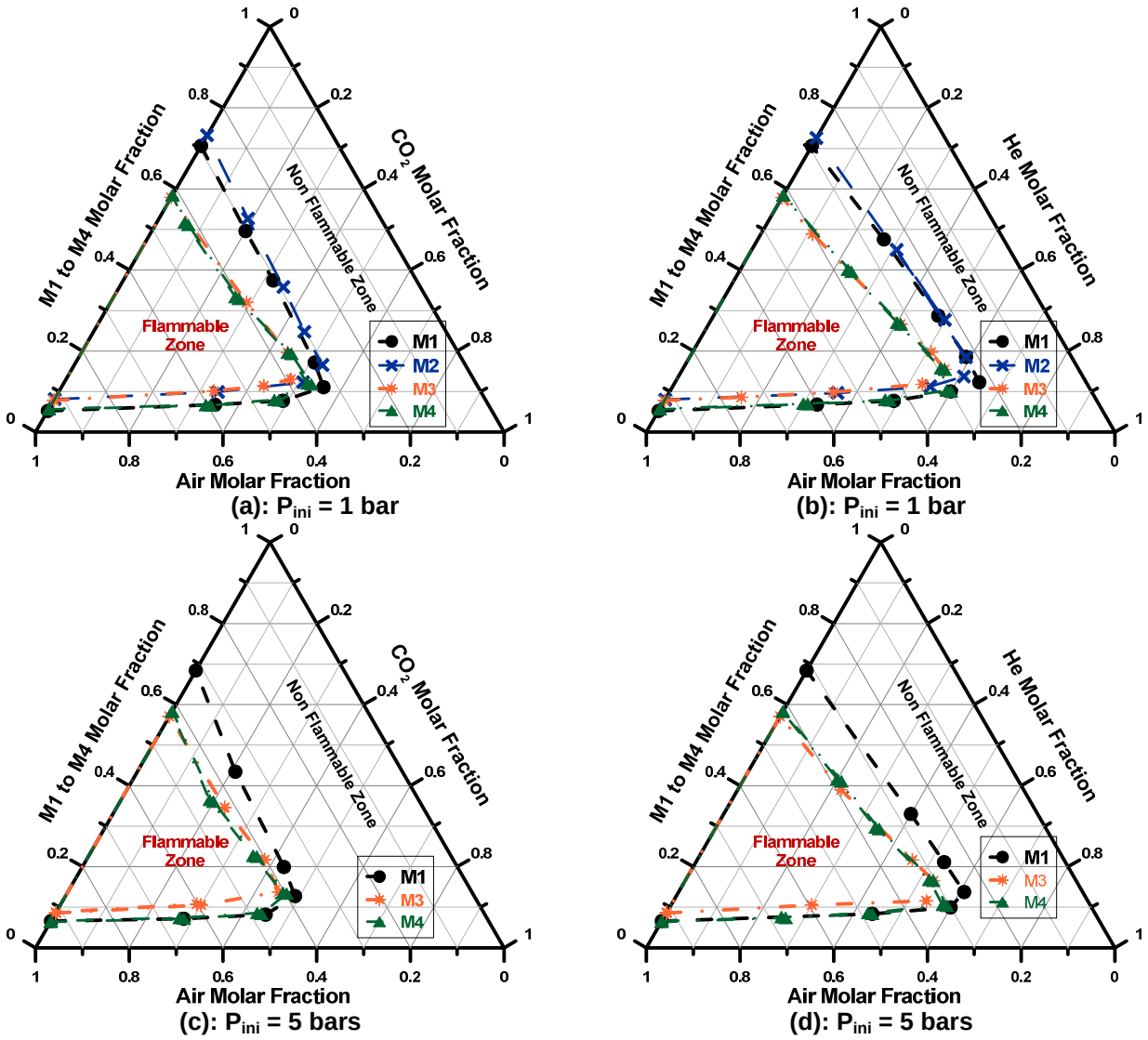


Figure 35: M1 to M4 Flammability domain according to the initial pressure and to the diluent type (He or CO2) measured at an initial temperature of 26℃.

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