

# Determination of flammability limits of diluted H<sub>2</sub>/CO/CH<sub>4</sub>/air mixtures in spherical bomb

R. Grosseuvres<sup>1,2</sup>, A. Comandini<sup>1</sup>, J. Biet<sup>1</sup>, M. Idir<sup>1</sup>, A. Bentaib<sup>2</sup>, N. Chaumeix<sup>1</sup>

<sup>1</sup>ICARE CNRS, 1C av de la recherche scientifique, 45000 Orléans, France

<sup>2</sup>IRSN, 31 av de la division Leclerc, 92262 Fontenay-aux-Roses

## 1 Introduction

The high temperature gas-cooled reactors (HTGRs) are graphite-moderated, helium-cooled reactors worldwide used for electricity and heat generation. The primary system of a HTGR consists of the reactor pressure vessel, the steam generator vessel, and the hot gas duct. In case of the rupture of a heat transfer tube of the steam generator, water may enter into the reactor pressure vessel. Due to the relatively high temperatures reached inside the reactor, steam can easily oxidize the graphite from both the fuel elements and the graphite structures and lead to the formation of He-H<sub>2</sub>-CO-CO<sub>2</sub>-H<sub>2</sub>O-CH<sub>4</sub> mixtures. Subsequently the pressure inside the reactor can increase exceeding the design pressure and leading to the opening of safety valves to the reactor hall. Hence, part of the combustible mixture could be released inside the reactor hall forming a flammable atmosphere. In order to assess the explosion hazard of such complex mixtures, flammability limits were investigated within the framework of the ARCHER (Advanced High-Temperature Reactors for Cogeneration of Heat and Electricity R&D) project.

Previous work has been devoted to flammability limits of the individual components (CH<sub>4</sub>, H<sub>2</sub>, CO) in air [1, 2, 3]. The effect of dilution was also studied for example with carbon dioxide or water vapor [4, 5]. On the other hand, no data are available for their mixtures diluted in helium or carbon dioxide. Thus, the aim of this study is to determine the flammability limits of 4 mixtures containing different amount of those components and investigate the dilution effect. Results were obtained for initial temperature of 300 K and pressure of 100 kPa or 500 kPa. The experimental data are visualized on ternary diagrams and compared in order to assess the influence of the various parameters (initial pressure, diluent, mixture composition) on the flammability domain.

## 2 Materials and experimental procedure

The experiments were conducted in a spherical bomb made of stainless steel, having a volume of 8 Litres and an internal diameter of 250 mm [6, 7]. A high frequency pressure transducer (Kistler 601AQO4 ; ± 0.1% full scale ; 0-50 bar abs) is mounted flush with the inner wall to measure any pressure increase due to a successful ignition. In order to measure the bomb temperature before each run, a thermocouple is placed against the outer wall. For most of experiments, the ignition is triggered by a laser spark at the center [6]. A variable attenuator is used in order to regulate the deposited laser

energy. For few experiments, an electrical discharge is produced by two tungsten electrodes (diameter 2mm), linked to a high voltage source and adapted probes to monitor the input power.

To observe the flame propagation or its extinction, a Z-type Schlieren arrangement [6] is used in the present experiments. A high speed camera (Phantom V1210) is used to monitor the occurrence of the combustion (flame recording) or to assess that the local ignition does not generate a sustainable flame and that the flammability limit is reached.

The compositions of H<sub>2</sub>/CO/CH<sub>4</sub> mixtures, Saphir grade, supplied by Air Liquide are reported in Table 1.

Table 1: Composition of the studied mixtures

Mixtures	CH <sub>4</sub>	H <sub>2</sub>	CO
Mixture M1	0 %	67.70 ± 1.35 %	32.30 ± 0.65 %
Mixture M2	0 %	31.66 ± 0.63 %	68.34 ± 1.37 %
Mixture M3	3.74 ± 0.08 %	30.56 ± 0.61 %	65.70 ± 1.31 %
Mixture M4	2.68 ± 0.05 %	65.83 ± 1.32 %	31.50 ± 0.63 %

Mixtures M1 and M2 have respectively compositions which are close to the ones of M4 and M3, the only difference being a small amount of methane added to the latter mixtures. For all the experiments, compressed dry air, helium (Air Liquide 99.999%) and carbon dioxide (Air Liquide ≥99.95%) were used.

## 2-2 Experimental procedure

In this study, flammability limits were determined by visual inspection of flame propagation. For each fuel and specific equivalence ratio, flammability limits were determined by varying the carbon dioxide or helium dilution percentage. Experiments were conducted at an initial temperature of approximately 300 K and initial pressures of 100 kPa and 500 kPa. For each run, a common systematic procedure was implemented. First, the spherical vessel bomb and the gas introduction lines were pumped down to less than 200 Pa by a primary pump. Before the injection of the gases and preparation of the mixture, the bomb temperature was recorded using the thermocouple. Then, fuel, air, and diluent were introduced in this order and the partial pressures measured with a MKS capacitive manometer connected to the introduction lines. Two different manometers were used based on the initial pressure in the bomb, the first with a pressure range between 0 and 100 kPa and the second between 0 and 1 000 kPa. Once the mixture preparation was established, the bomb was isolated by closing the gas introduction line. The attenuator was adjusted in order to deposit a minimal energy at the center of the bomb and the laser was triggered. If the mixture did not ignite, the deposited energy was increased by modifying the attenuator angle and the laser was triggered again. For each specific equivalence ratio and dilution, the laser energy was gradually increased from 20 mJ until 90 mJ or until flame propagation. For each laser energy, 5 attempts were conducted successively. If the mixture did not ignite for a specific equivalence ratio and dilution, this procedure was repeated in order to make sure the mixture is non flammable. While keeping this procedure, the laser was substituted by electrodes for the study of mixture M2 at 5 bars.

Four different behaviours were observed during the experiments. First the extinction of the flame could occur, as shown in Figure 1-a. Local disturbance, related to the ignition by the spark, dissipates quickly and no pressure increase is noticed. In this case, heat production is less important than heat losses, thus no flame propagation is observed [8]. The spark ignition can also result of a quenched flame, where flame appearance occurs but without further propagation (Figure 1-b). On the other hand, inside the flammability domain, the ignition can result in an ascendant flame (Figure 1-c) or a spherical flame (Figure 1-d) according to the percentage of fuel present in the initial mixture. The size

of an ascendant flame gradually increases during its propagation as in Figure 1-c although the pressure can increase only slightly or remain constant since the combustion is incomplete and limited to only a fraction of the available volume. For a spherical flame, the pressure increase is important and reaches the value corresponding to the combustion of the total volume. The maximum pressure in this case is very close to the theoretical one corresponding to an adiabatic isochoric complete combustion ( $P_{AICC}$ ).

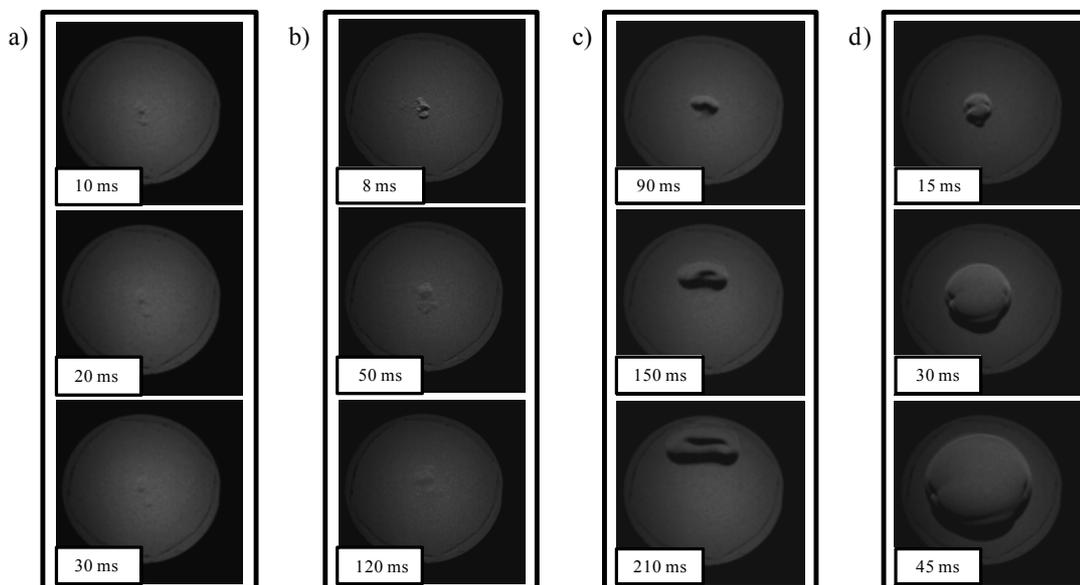


Figure 1: Snapshots of different behaviors observed for Mixture M3 at 500 kPa initial pressure. a: 296K with Helium dilution; b: 295K without diluent; c: 302K with Helium dilution; d: 298K with Helium dilution

### 3 Experimental results

The flammability limits measurements of the four studied mixtures are presented here in ternary diagrams. The points represent the last non flammable mixtures before reaching the flammable domain from the non flammable domain. They were found by setting equivalence ratio and rising the dilution percentage. The first part of the analysis will deal with the effect of the pressure and the dilution while the second part will concern the flammability domain dependence on mixture composition.

#### 3-1 Pressure and dilution effects on flammability limits

Figure 2 presents the flammability diagrams of the four mixtures diluted in helium or in carbon dioxide, for both initial pressures: 100 kPa and 500 kPa. First, we can notice that for both cases of dilutions, pressure increase from 100 kPa to 500 kPa lead to a reduction in the flammability domain except for the mixture M2 diluted in helium. While the upper flammability limits are not strongly affected, the lower flammability limits can change significantly (almost +26%Fuel for Mixture 1). It has been observed that a variation of the initial pressure has an effect which is specific for each flammable mixture [1]. We can also observe that the dilution with carbon dioxide leads to smaller flammable domain compares to the case with helium dilution. As its specific heat is greater (37.12 J/mol.K against 20.79 J/mol.K at 298K), carbon dioxide is a better inert substance than helium. This result is in agreement with previous studies on the extinction efficiency of these diluents [1, 8].

Except for the upper flammability limits, the upper boundaries of each fuel mixture are greatly affected by the initial pressure or diluent. Excluding the mixture M2 diluted in helium, in each case the upper boundaries are reduced when the pressure rises or when carbon dioxide is used as diluent.

### 3-2 Composition effect on flammability domain

The flammability domains of the four mixtures in each condition of pressure and dilution are reported in Figure 3. A comparison can easily be performed to highlight the effects of the fuel composition on the flammability behaviour.

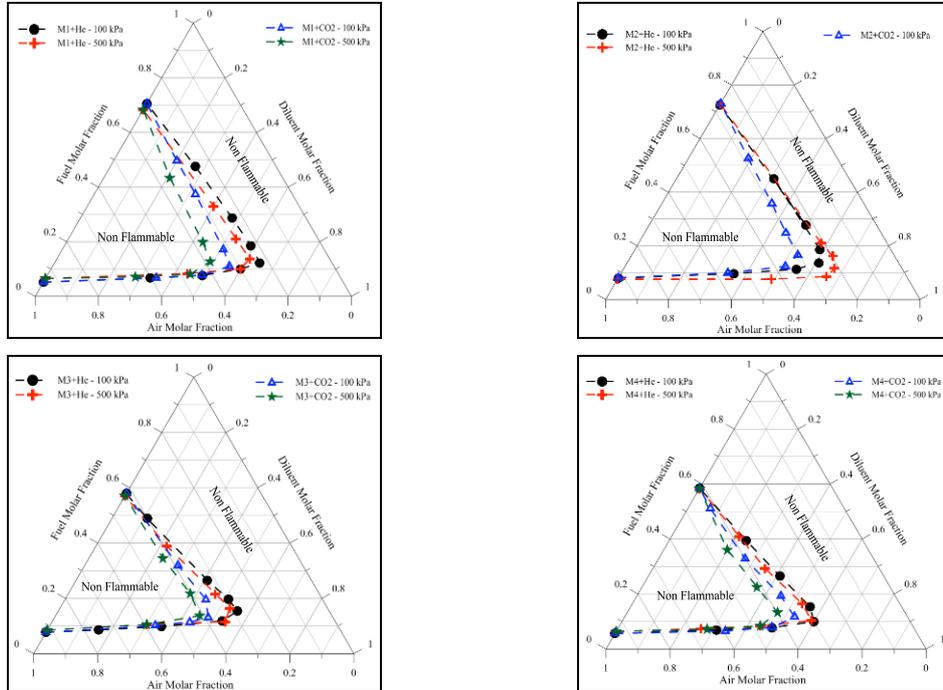


Figure 2: Flammability diagrams of each mixture diluted in helium or carbon dioxide, at 100 kPa and 500 kPa

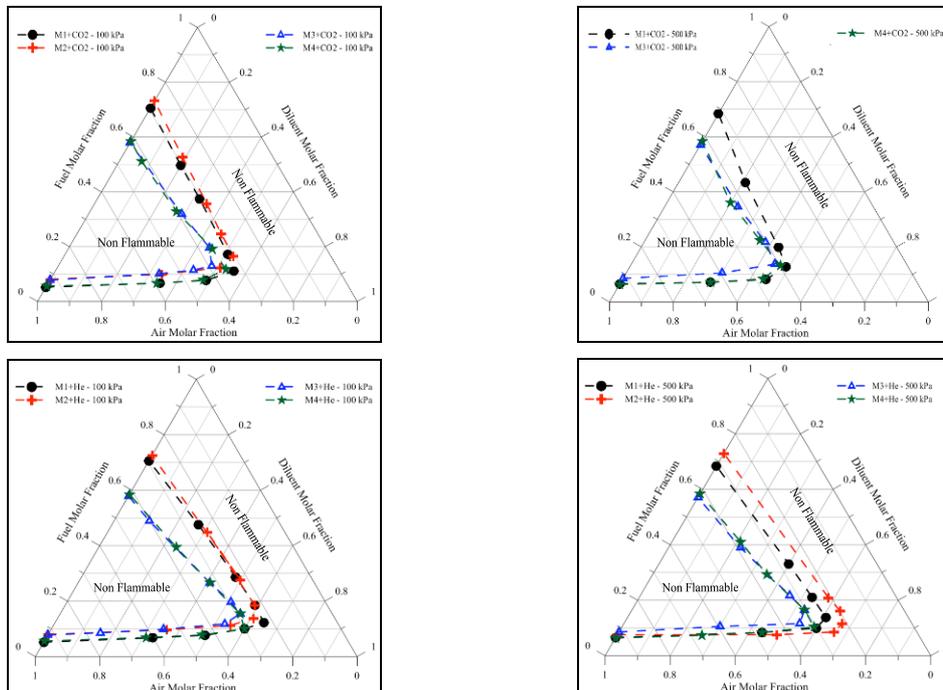


Figure 3: Comparison of flammability domains of the four mixtures at 100 kPa and 500 kPa, diluted in carbon dioxide or helium

Figure 3 shows that mixtures M3 and M4 which contain CH<sub>4</sub>, have a smaller flammability domain than Mixtures M1 and M2. The addition of CH<sub>4</sub> impacts mainly the upper boundaries. For instance, mixtures M1 and M4 diluted in helium at 100 kPa have closed lower branch but they differ in the upper branch (between 25 and 43%Fuel of difference). The same comment can be done between mixtures M3 and M2. For each condition, the mixture M3 which have the greatest amount of methane and the smallest amount of hydrogen, has the narrower flammability domain. These observations are in agreement with the well-known flammability limits of each component of the four mixtures. Indeed, the flammability domain of methane (5-15%Vol. in air) is less important than the one of hydrogen (4-75%Vol. in air) [8].

Furthermore, Figure 3 allows to deduce the minimum diluent volumic fraction in order to inhibit any flame ignition and propagation for each mixture and for both initial pressures. Table 2 reports this diluent volumic fraction for each case of this study.

Table 2: Minimum diluent volumic fraction to inhibit combustion for the studied mixtures at 100 and 500 kPa

	100 kPa		500 kPa	
	He (%Vol.)	CO <sub>2</sub> (%Vol.)	He (%Vol.)	CO <sub>2</sub> (%Vol.)
Mixture M1	64.92 ± 0.04	55.92 ± 0.04	60.96 ± 0.64	49.00 ± 0.60
Mixture M2	60.94 ± 0.04	52.93 ± 0.04	Not analyzed	Not analyzed
Mixture M3	55.93 ± 0.04	47.99 ± 0.04	53.98 ± 0.62	45.02 ± 0.58
Mixture M4	60.00 ± 0.03	53.00 ± 0.03	58.96 ± 0.64	46.92 ± 0.59

Finally, lower and upper flammability limits experimentally obtained are compared to theoretical data obtained with the Le Chatelier's formula [9]. This formula is commonly used to predict the flammability limits of blended gases with similar properties. Table 3 presents a comparison between the mixtures limits achieved in this study and calculated limits for the same mixtures at 100 kPa. Differences, between calculated and experimental lower limits, are low (less than 1%). Experimental limits are always more important than the theoretical ones. Concerning the upper flammability, differences more important can be noted (up to 8.99% for the mixture M4). But here the experimental limits are always lower than the theoretical ones. Thus, Le Chatelier's formula seems to be a good approximation of the lower and upper flammability limits.

Table 3: Comparison between calculated and experimental Upper and Lower Flammability Limits of the studied mixtures (100 kPa)

	Lower Flammability limit (%Vol. Fuel)		Upper Flammability limit (%Vol. Fuel)	
	Theory	Experiment	Theory	Experiment
Mixture M1	5.12	5.22 ± 0.03	74.74	70.61 ± 0.05
Mixture M2	7.46	8.01 ± 0.03	74.45	73.21 ± 0.05
Mixture M3	7.32	7.89 ± 0.03	64.73	57.90 ± 0.04
Mixture M4	5.12	5.61 ± 0.02	67.48	58.49 ± 0.03

## 4 Conclusions

Experiments on flammability limits were conducted in spherical vessel for four mixtures initially at 300 K, for 2 initial pressures: 100 kPa and 500 kPa. The mixtures contained H<sub>2</sub>, CO and CH<sub>4</sub> in different amounts. First, the study concerned the dilution and initial pressure effects on flammability limits. It has been shown that carbon dioxide dilution is more effective in suppressing the combustion than helium. The reduction of the flammability domain produced by rising initial pressure was also observed except for one mixture (M2). The study concerned then the composition effect on flammability domain. The addition of CH<sub>4</sub> in the mixtures showed a decrease of the flammability domains. Then a minimum diluent molar fraction to suppress any combustion was found for each mixture. Finally, it was found that Le Chatelier's formula permits to approach the lower flammability limits but does not apply for the upper flammability limits.

In this study, the measurements of the inflammability limits of mixture M2 diluted in carbon dioxide at 500 kPa were not conducted. The study will be completed in a near future.

## Acknowledgment

This work has been funded by the EC within the ARCHER (Advanced High-Temperature Reactors for Cogeneration of Heat and Electricity R&D) project.

## References

- [1] Coward HF, Jones GW. (1952). Limits of flammability of gases and vapors. Bureau of Mine. 503: 114.
- [2] Cashdollar KL, Zlochower IA, Green GM, Thomas RA, Hertzberg M. (2000). Flammability of methane, propane, and hydrogen gases. *Journal of Loss Prevention in the Process Industries*. 13: 327.
- [3] Cheikhvat H, Chaumeix N, Bentaib A, Paillard C-E (2012). Flammability limits of hydrogen-air mixtures. *Nuclear Technology*. 178: 5.
- [4] Kumar RK. (1985). Flammability Limits of Hydrogen-Oxygen-Diluent Mixtures. *Journal of Fire Science*. 3: 245.
- [5] Cheikhvat H, Goulier J, Bentaib A, Meynet N, Chaumeix N, Paillard C-E (2015). Effects of water sprays on flame propagation in hydrogen/air/steam mixtures. *Proceedings of the Combustion Institute*. 35: 2715.
- [6] Biet J, Ndem M, Idir M, Chaumeix N. (2014). Ignition by Electric Spark and by Laser-Induced Spark of Ultra-Lean CH<sub>4</sub>/Air and CH<sub>4</sub>/CO<sub>2</sub>/Air Mixtures at High Pressure. *Combustion, Science and technology*. 186(1): 1.
- [7] Mével R, Lafosse F, Chaumeix N, Dupré G, Paillard CE. (2009). Spherical expanding flames in H<sub>2</sub>-N<sub>2</sub>O-Ar mixtures: flame speed measurements and kinetic modeling. *International Journal of Hydrogen Energy*. 34: 9007.
- [8] Glassman I. (1987). *Combustion* Second edition. Academic Press, Inc, London, 141.
- [9] Le Chatelier H, Boudouard O. (1898). Limits of flammability of gaseous mixtures. *Bulletin de la Société Chimique*. 19: 483.