Experimental flammability limits of H_2–CO–CO_2-air mixtures and kinetic model simulation

A. Palomino[1]*, M, Comito[1], A. Mendy[1], A. Bentaib[2], A. Comandini[1], N. Chaumeix[1]
[1]ICARE, UPR 3021 CNRS, Orléans, France
[2]ISNR, Fontenay-aux-Roses, France

1 Context

The flammability limits of fuel mixtures are crucial for fire prevention, assessing explosion risks, and designing protective systems. These limits define the range of combustible/oxidizing mixtures in which flame propagation is possible when an external ignition source is introduced. The two key flammability limits are the lower flammability limit (LFL), also known as fuel-lean, and the upper flammability limit (UFL), or fuel-rich [1]. Several studies have examined the flammability limits of the H_2–CO mixture in air [2–5], the effect of dilution—such as with carbon dioxide or nitrogen—has also been explored [6, 7]. However, the reported data can differ by more than 5% in fuel composition. These variations are often due to the different criteria used to determine the flammability limits, whether visual or pressure-based. Other factors, such as temperature, pressure, ignition source, and the type and volume of the container, can also influence the results. In this study, the experimental flammability limits are determined for a 50% H_2–50% CO mixture in air, with CO_2, at 298 K and 1 bar. The increase in pressure within the container is used as the criterion for assessing fuel flammability. To avoid false positives or negatives, a parametric logistic distribution function is employed to calculate the flammability limits and [8]. Additionally, a flame speed sensitivity analysis of H_2–CO–CO_2–air mixtures provide insight into the effects of the diluent on chemical kinetics near the LFL.

2 Methodology

2.1 Experimental setup

A spherical stainless-steel vessel is used for the flammability experiments. The volume and internal diameter of the vessel are 8 L and 250 mm, respectively. The vessel has two optical access quartz windows (60 mm). The spherical vessel and all its accessories are designed to withstand a maximum working overpressure of 50 bar. An external electrical heating system allows to control the temperature between 298 K and 373 K. The vessel has a sufficient number of ports for filling, emptying and purging. The pressure measurement system to record the overpressure during the combustion, consists of a high-frequency pressure transducer (Kistler 601A, maximum pressure 250 bar, acquisition frequency of 150 kHz), an amplifier (Kistler Type 5011), and one oscilloscope as recording device of the combustion pressure (Wavesurfer 3024 200 MHz 4GS/s). The lowest range of the pressure transducer is 0.1bar/V.

Correspondence to: alejandra.palomino@cnrs-orleans.fr

The partial pressure method is used to prepare the mixture fuel – inert gas – oxidant. To prepare the mixtures, the vessel is equipped with two vacuum pumps and two pressure manometers, Edwards 6000AB 750Torr and Omega 1bar. The gases hydrogen – carbon monoxide (H_2 = 50.0335% and CO = 49.9665%), carbon dioxide (CO_2=99.9999%) and air (O_2 = 20.90% and N_2 = 79.10%) are provided by Air Liquide. CO2 is used as diluent. A high-speed camera (Phantom Micro C110) was used to visualize the propagation of the flame.

The ignition source is manufactured in according to NF EN 1839, March 22, 2017 [9]. A series of sparks are induced by tungsten electrodes in alternating current using a high voltage transformer; the total energy emitted by the sparks in air is around 2 J and the average discharge time is 0.2 s. The electrodes are spaced at ± 5.0 mm. Voltage and current measurements are made possible by Tektronix P6015A high voltage probe and current transformer (Magnelab, CT-B 0.1-BNC 10 – 50 MHz 0.1 volt/Amp). Measurements are recorded by a digital oscilloscope (Rohde & Schwarz RT2004 2.5 GS/s). The synchronization between the acquisition scopes, the pressure transducer and the camera with the spark creation is obtained by using a pulse generator (SRS DG 235).

2.2 Flammability criterion

A mixture is considered flammable when an overpressure equal or higher than 5% of the initial absolute pressure created by the ignition source is generated in air [9]. A parametric logistic distribution equation (y) is used to avoid any false true signal. If the overpressure is equal or higher than 5%, the mixture is considered flammable and is assigned a probability value of y=1, otherwise when the pressure increase is less than 5%, the probability value of the test is y = 0 [8].

Parametric logistic distribution equation: $y = \frac{1}{1+\exp(-a-bx)}$

where x is the fuel content and a and b are coefficients.

2.3 Experimental procedure

Prior to each experiment, the vessel is purged with air and pumped to a residual pressure of 0.1 torr. The vessel and feed lines are heated to 298 K. The components of the mixture are introduced one after the other into the vessel according to their partial pressures. The order in which the compounds are introduced is fuel, inert gas and oxidizer. The initial total pressure is 1 bar. The feed lines are purged each time a component is introduced. The composition of the mixture depends on the flammability limit to be evaluated. After 3 minutes of preparing the mixture, all access valves to the vessel are closed and the ignition source is activated. Pressure vs. time, voltage vs. time and current vs. time curves are recorded. After ignition, the gases are pumped out of the vessel for the next experiment. Additional experiments are carried out near the limit and the probability is calculated using the parametric logistic distribution equation. The flame temperature (T_{fl}) and the adiabatic isochoric complete combustion pressure (P_{AICC}) of mixtures H_2–CO–CO_2–air and sensitivity analysis of the flame speed are calculated using COSILAB [10]. The kinetic mechanism and the thermodynamic and transport properties of all the species and radicals involved during combustion are obtained from the literature [11].

3 Results

3.1 Flammability limits

The flammability limits of H_2–CO in air at standard conditions are widely known in the open literature. The lower limit is around 6% and the upper limit around 73% [2]. These values are taken as a reference for the first experiments. In the LFL zone, a small increase of H_2–CO in the mixture (0.5%) produces a gradual increase in combustion pressure (about 7%), while a similar increase of fuel in the rich zone generates an overpressure 3 times higher than the initial pressure (Fig. 1). This can be attributed to the fact that close to the LFL, the high diffusivity of H_2 lead to a combustion of the mixture aided by gravity leading to a flame propagation only in the upward direction. At the UFL side, the combustion is dominated by the diffusion of O_2 and hence the preferential diffusion of the fuel does not play a role.

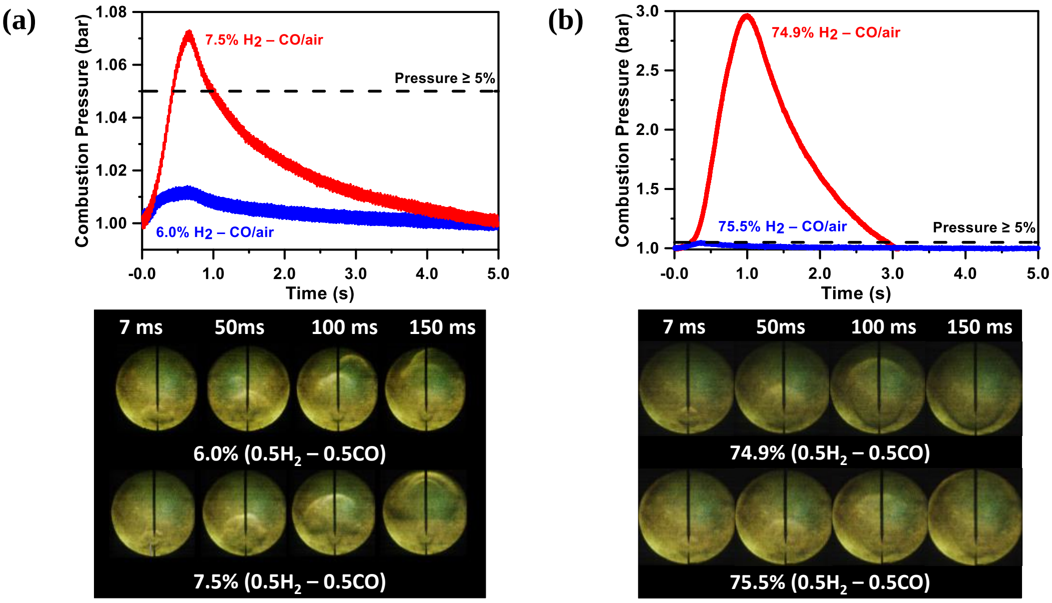

Figure 1. combustion pressure vs time of H_2–CO in air at 298 K and 1 bar. (a): LFL and (b): UFL

Once the fuel content range is found in which the mixture goes from non-flammable to flammable, additional experiments are carried out to establish the combustion regime characterized by the temporal evolution of the experimental pressure (Fig. 2). The experimental combustion pressure remains much lower than the theoretical one since the flam propagates mainly in the upward direction leading to an incomplete combustion. As the fuel is increased in the mixture, the experimental combustion pressure rises since the flame propagation lead to a combustion of a larger part of the fresh gases until reaching a complete combustion when the content of the fuel reaches 8%. On the rich side, the below 75.5 % of fuel, the flame is dominated by buoyancy leading to an incomplete combustion as well. The minimum T_{fl} for a flammable mixture in the LFL zone is 850 K, while in the UFL zone, it is higher than 1150 K.

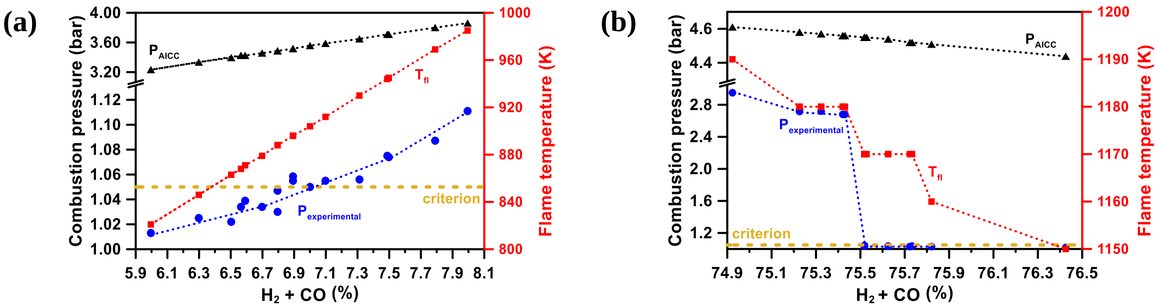

Figure 2. Evolution of the P_{AICC}, flame temperature and maximum experimental pressure at 298 K and 1 bar. (a): LFL and (b): UFL

The flammability limit is the 1% of the logistic equation, this (Fig. 3a and 3b). LFL of H_2–CO in air in the literature is between 5.0% and 7.3 %, while ULF is in the range of 71 % – 74% [3, 5 – 7]. These differences with respect to the flammability limits found in this study can be attributed to the deposited ignition energy and the flammability criterion. In this study, the deposited ignition energy is higher than

2 J, while in the literature lower ignition energies are reported, between 20 mJ and 80 mJ. Likewise, different criteria are applied, such as the visual or overpressure limit of 2% and 7% [2, 3, 12].

3.2 Dilution effect

The flammability diagram for H_2–CO–CO_2–air at 298 K and 1 bar are shown in Fig. 3c. As the amount of CO_2 in the mixture increases the flammability range decreases: (1) LFL increases from 6.47% ± 0.07% (non-diluted) to 8.12 % ± 0.07 % with 50 % CO_2 and (2) UFL decreases from 75.6% ± 0.06% (non-diluted) to 19.9 % ± 0.07 % with 50%CO_2. The atmosphere will be rendered non-flammable irrespective of the content of fuel for H_2–CO–air mixtures, with $CO_2 \geq 57.7$ %. The inert point of the mixture corresponds to equivalent ratio $\varphi = 0.85$.

In the UFL line, the available oxygen content increases from 5.1% to 6.5% with increasing CO_2 content; while in the LFL line, the oxygen content decreases from 19.5% to 6.5% with increasing inert gas.

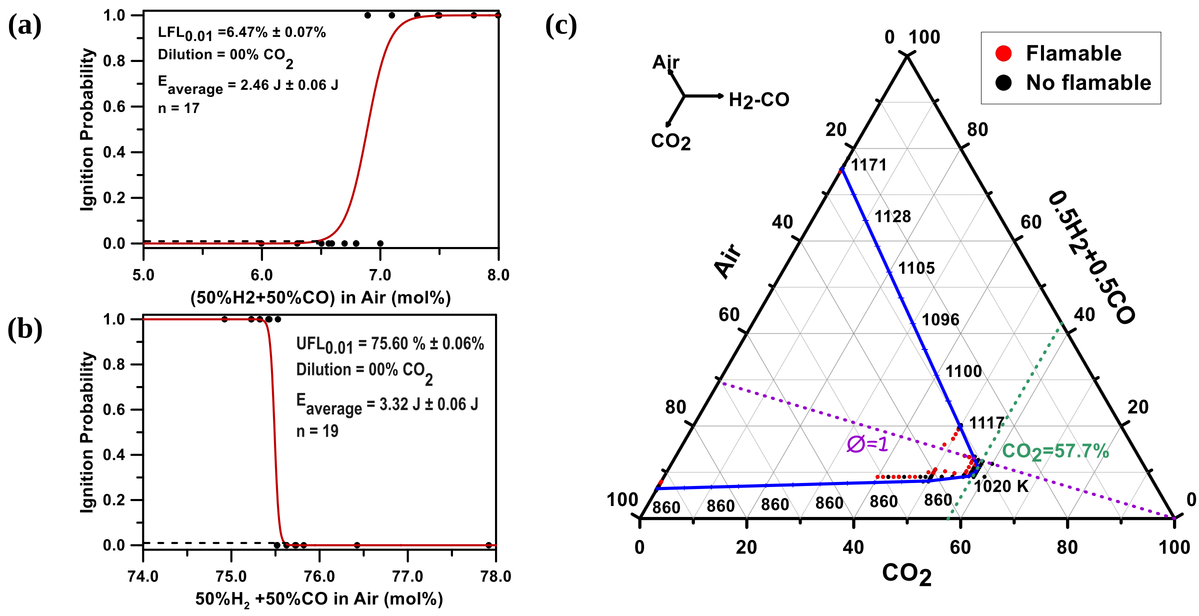

Figure 3. Ignition probability of H_2–CO–air at 298 K and 1 bar. (a): LFL, (b): UFL and (c) Flammability diagram of H_2–CO–CO_2–air at 298 K and 1 bar.

3.3 Kinetics model results

The effect of inert gas on the chemical kinetics near the LFL is analyzed using COSILAB and the USC mechanism. The fractions of OH, O and H radicals are significantly reduced by the addition of CO_2, while H_2O_2 and HO_2 radicals had a higher participation in the combustion by the addition of inert gas (Fig. 4). Near the lower limit, the H_2 content is very low (≤ 5%), which decreases the content of H free radicals. Likewise, with the addition of CO_2, the oxygen content is reduced by half, which affects the amount of O free radicals involved in the reactions generating OH radicals. The H and OH radicals intervene in the branching and propagation elementary reactions, that contributing to the explosive nature of the combustion. The CO_2 also decreased the flame temperature and therefore, contributed to the significant reduction of OH, O and H radicals and the inhibition of flame propagation.

The flame speed sensitivity analysis for H_2–CO–CO_2–air mixtures using COSILAB and the USC mechanism. are shown in Fig. 5. The sensitivity analysis allowed to understand the effect of CO_2 on the chemical kinetics near the lower flammability limit. The inert gas disrupts the main chain reaction pathway of the H_2–CO combustion process: (1) it increases the sensitivity of the elemental reaction

O_2+H=O+OH and (2) it decreases the sensitivity of the reaction CO+OH=CO_2+H. H_2 reacts mainly with O radicals to generate OH and H; its positive effect on flame propagation decreases with the addition of CO_2.

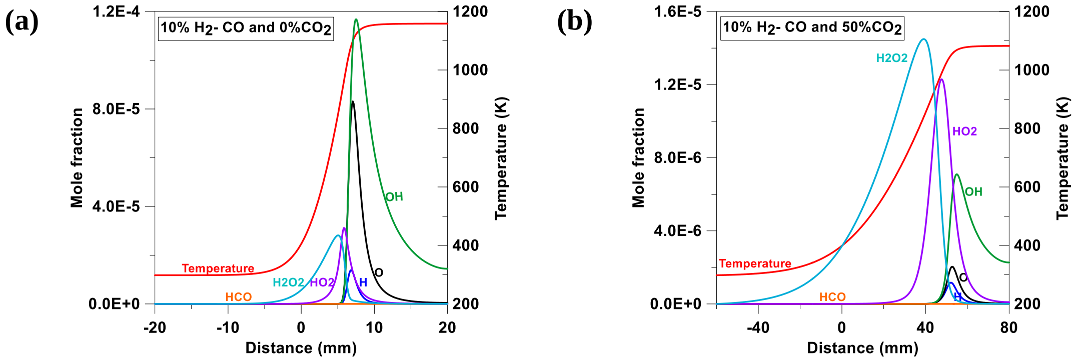

Figure 4. calculated mole fractions of the radicals of H_2–CO–air combustion close to LFL at 298 K and 1 bar. (a): 0%CO_2 and (b): 50%CO_2

The H radical enables branching and propagation of combustion from the reactions H+O_2=O+OH and H+HO_2=2OH, these reactions being more significant with increasing dilution and fuel and have a positive effect on flame speed. The OH radical generated by the reactions of H_2 and H facilitates the chemical transformation of CO into CO_2. The reaction CO + OH = CO_2 + H, is the main pathway in which CO and CO_2 participate. However, the inert gas has an inhibitory effect on the oxidation of CO, due to the reduction of oxygen in the mixture that favors the reverse reaction (CO_2 + H = CO + OH), consuming H radicals [13]. The OH is a crucial radical throughout the chain reaction, as it also promotes the chemical conversion of H_2 to H_2O (H_2 +OH = H_2O + H).

The increase in HO_2 radicals, for mixtures with fuel contents close to the LFL and especially when CO_2 is added, increases the effect on the reactions OH +HO_2 = O_2 +H_2O, O +HO_2 = H+H_2O and O +HO_2 = O_2 +OH, which contribute to the termination of combustion.

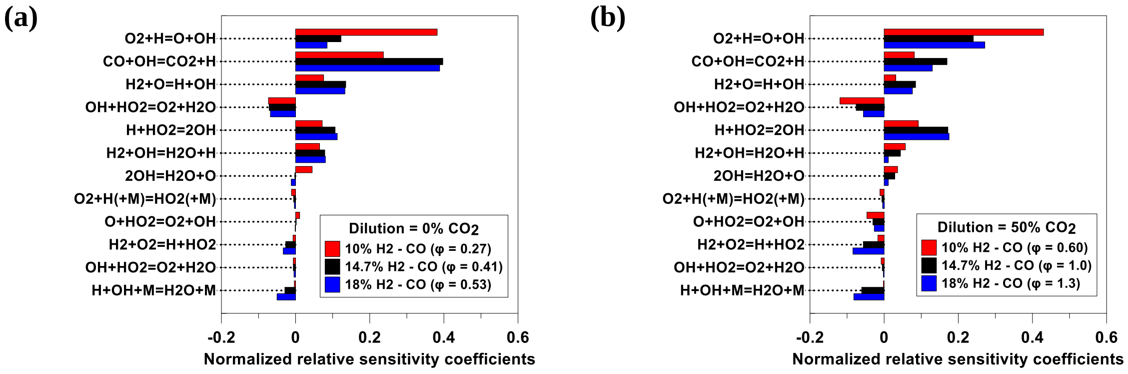

Figure 5. Flame speed sensitivity coefficients for the top 12 most sensitive reactions at 298 K and 1 bar. (a): 0%CO_2 and (b): 50%CO_2

4 Conclusions

The experimental flammability limits are determined for a mix 50% H_2 – 50% CO in air with CO_2 as inert gas at 298 K and 1 bar. The energy deposited by the sparks (more than 2 J) and the flammability criterion may be the reason for the variability between the different flammability values available in the literature and those reported in this study. It is concluded that the chemical kinetics can be considerably diverged with the addition of CO_2, especially close to the LFL.

Acknowledgement

The work was part of the AMHYCO project, which received funding from the Euratom research and training program 2019-2020 (Grant n°945057). The content of this paper reflects only the authors' view. The European Commission is not responsible for any use that may be made of the information it contains

References

[1] McAllister, S., Chen, JY., Fernandez-Pello, A.C. (2011). Premixed Flames. In: Fundamentals of Combustion Processes. Mechanical Engineering Series. Springer, New York, NY.

[2] Coudoro, Kodjo. (2012) Etude expérimentale et modélisation de la propagation de flamme en milieu confiné ou semi-confiné. Doctorat de l’université d’Orléans. p. 24.

[3] Grosseuvres, R. and Comandini, A. (2015). Determination of flammability limits of diluted H_2-CO-CH4-air mixtures in spherical bomb. 25th ICDERS.

[4] Shang, R; Li, G. and Wang, Z. (2020). Lower flammability limit of H_2/CO/air mixtures with N_2 and CO_2 dilution at elevated temperatures. International Journal of Hydrogen Energy 45

[5] Shang, R.; Zhuang, Z.; Niu, J.; Han, Q.; Li, G. and Zhang, P. (2023). Experimental study on the lower flammability limit of N_2 and CO_2 diluted H_2/CO/air mixtures at high initial pressure. International Journal of Hydrogen Energy 48.

[6] Li, Rui; Liu, Zhenyi and Mingzhi, Li. (2022). Investigation on the flammability limit and limiting oxygen concentration of N_2-diluted H_2/CO/air mixtures at high temperature and pressure. Fuel 308.

[7] Van den Schoor, F.; Norman, F.; Vandermeiren, K.; Verplaetsen, F.; Berghmans, J. and Van den Bulck, E. (2009). Flammability limits, limiting oxygen concentration and minimum inert gas/combustible ratio of H_2/CO/N_2/air mixtures. International Journal of Hydrogen Energy 34, 4, 2069-2075.

[8] Bane.S. (2010). Spark Ignition: Experimental and numerical investigation with application to aviation safety. California Institute of Technology, Pasadena, California

[9] Normes françaises et européennes. (2017). Détermination des limites d'explosivité des gaz et vapeurs et détermination de la concentration limite en oxygène (CLO) des gaz et des vapeurs inflammables (NF EN 1839)

[10] COSILAB, The combustion simulation laboratory. (2021). Version 4.3.2. Rotexo GmbH & Co. KG. Bochum, Germany. http://www.SoftPredict.com.

[11] Scott, Davis; Ameya, Joshi and Hai, Wang. (2003). H_2/CO high temperature Combustion Mechanism. Department of Mechanical Engineering, University of Delaware, Neark, DE 19716

[12] ASTM international. (2015). Standard Test Method for Concentration Limits of Flammability of Chemicals (Vapors and Gases) (E681 -09)

[13] Su, B.; Dong, H.; Luo, Z.; Deng, J.; Liao, P.; Cheng, F., Wang, T.; Liu, L.; Liu, L. (2024). Effects of H_2/CO ratio and CO_2 dilution on the explosion behavior and flame evolution of syngas/air mixtures. International Journal of Hydrogen Energy 69. 451-465.