

FLAMMABILITY OF SYNGAS/CO₂ MIXTURES IN OXYGEN-ENRICHED AIR

V. Di Sarli*, A. Basco*, F. Cammarota*, A. Di Benedetto**,
E. Salzano*

almerinda.dibenedetto@unina.it

* Istituto di Ricerche sulla Combustione, CNR, Via Diocleziano 328, 80124, Napoli, Italy

** Dipartimento di Ingegneria Chimica, Università di Napoli Federico II

Abstract

The un-stretched laminar burning velocity of H₂/CO/O₂/N₂/CO₂ mixtures has been evaluated either experimentally or numerically, by means of the CHEMKIN package coupled to the detailed Davis reaction scheme. The effect of CO₂ was demonstrated to be essentially thermal. Some compositions show anomalous impulses that can be explained on the basis of the phenomenon of combustion-induced Rapid Phase Transition (c-RPT).

Introduction

Syngas can be produced by traditional hydrocarbon steam reforming or gasification of a wide range of solid combustibles, including carbon, biomasses and wastes. The combination of oxy-combustion and syngas would certainly represent a further step towards environmental goals [1-5]. However, that implies new safety issues for the laminar burning velocity increase due to the higher reactivity and due to the dilution of syngas with CO₂, which results in substantial decrease of the same parameter [6].

In previous papers, we have evaluated the laminar burning velocity of CH₄/O₂/N₂/CO₂ and H₂/O₂/N₂/CO₂ stoichiometric mixtures [7]. The aim of the present study is the analysis of the combined effects of CO₂ and O₂ contents on the reactivity and explosion behavior of the same mixtures at different concentration, both experimentally and numerically by means of the CHEMKIN® package.

Results have confirmed previous findings on the thermal and kinetic role of CO₂. Furthermore, an anomalous behavior has been observed for mixtures with high content of hydrogen and oxygen and low concentration of CO₂. Indeed, peak overpressures up to ten times the adiabatic combustion pressure have been found. Such phenomenon has been recently explained and named “combustion-induced Rapid Phase Transition” (c-RPT) [8-12].

Experimental

The experimental set-up adopted in this study is shown in Figure 1. The main reactor is composed by an AISI 316 SS steel (MAWP=400 bar) cylindrical vessel (5 lt) with wall thickness of 5 cm. The mixture composition was obtained by the

partial pressure method at 1 bar and 300 K. Gases were premixed by mechanical stirring (rotating shaft velocity equal to 200 rpm). They were allowed to settle for around 30 s and then ignited by an electric spark (25 kV, 30 mA) positioned at the center of the vessel. Each test was performed 3 times. Pressure histories were recorded by KULITE ETS-IA-375 (M) series transducers powered by a chemical battery (12 VDC/7 Ah) in order to minimize any disturbance on the output supply, which was recorded by means of a National Instrument USB-6251 data acquisition system (1.25 Msamples/sec). Further details can be found elsewhere [8-12].

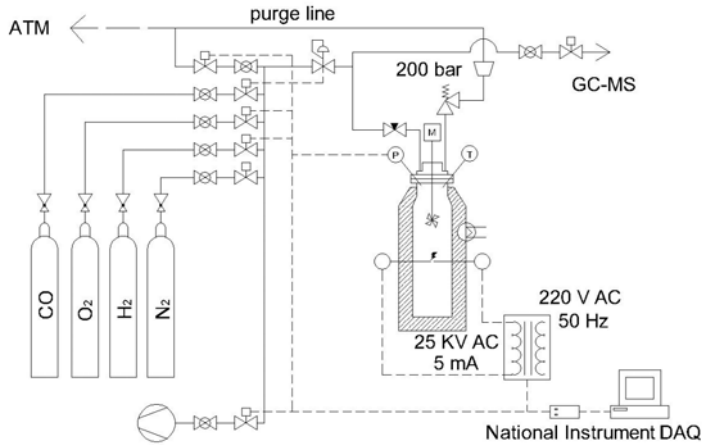


Figure 1. The experimental set-up adopted for this study.

The mixture compositions investigated are given in Table 1, together with the corresponding values of adiabatic temperature (T_{ad}) and pressure (P_{ad}) at constant volume, as computed using the GASEQ Chemical Equilibrium Program [13]. The equivalence ratio ϕ and the oxygen-enrichment factor E are defined as:

$$\phi = \frac{\left(\frac{H_2 + CO}{O_2} \right)}{\left(\frac{H_2 + CO}{O_2} \right)_{st}}; \quad E = \frac{O_2}{O_2 + N_2} \quad (1)$$

The laminar burning velocity was obtained from the time pressure record of the explosion occurring in the closed vessel. In particular, we used the equations of Dahoe et al. [14,15] that link the flame radius, r_f , and the laminar burning velocity, S_L , to the pressure time history.

The flame radius was calculated by using the following correlation:

$$r_f = \left(\frac{3V}{4\pi} \right)^{1/3} \left[1 - \left(\frac{P^o}{P} \right)^{1/\gamma} \left(\frac{P_{max} - P}{P_{max} - P^o} \right) \right]^{1/3} \quad (2)$$

where P_{\max} is the maximum measured pressure, P° is the initial pressure, and V is the vessel volume. The (un-stretched) laminar burning velocity, S_l , was then calculated according to:

$$S_l = \lim_{r_f \rightarrow 0} \left[\frac{d}{dt} r(t) \right]_{\Delta r_f} \quad (3)$$

where $r(t)$ is the best fit function in the range $\Delta r_f = (r_f - r_{f,0})$ that refers to the range of the flame radius for which either ignition or wall and vessel shape effects on the flame propagation can be neglected. The value of S_l corresponds to the un-stretched burning velocity as in Huang et al. [16].

Table 1. Mixture compositions analyzed in this work: Y is the molar fraction; P_{ad} is the adiabatic flame temperature and pressure as calculated using GASEQ [13] (Test 1: no CO_2 ; all others 40% CO_2). $E = \text{O}_2/(\text{O}_2 + \text{N}_2)$. P_{\max} and S_l are the maximum pressure and the laminar burning velocity found experimentally.

N	ϕ	H_2/CO	E , -	Y_{H_2} , -	Y_{CO} , -	Y_{O_2} , -	P_{ad} , bar	P_{\max} , bar	S_l , cm s^{-1}
1	1.00	1	0.21	0.148	0.148	0.148	7.9	6.31 ± 0.03	97.5 ± 8.2
2	1.00	1	0.21	0.089	0.089	0.089	5.2	4.15 ± 0.0	6.5 ± 1.9
3	1.00	1	0.60	0.164	0.164	0.164	6.9	5.67 ± 0.0	67.6 ± 2.8
4	1.00	2	0.21	0.118	0.059	0.089	5.2	4.08 ± 0.0	8.3 ± 2.7
5	1.00	2	0.60	0.218	0.109	0.164	6.9	6.16 ± 0.0	80.2 ± 7.1
6	1.75	1	0.21	0.127	0.127	0.073	4.5	3.29 ± 0.14	13.2 ± 1.7
7	1.75	1	0.60	0.203	0.203	0.116	6.0	5.16 ± 0.13	77.5 ± 8.4
8	1.75	2	0.21	0.169	0.085	0.073	4.5	3.42 ± 0.06	10.3 ± 0.6
9	1.75	2	0.60	0.271	0.135	0.116	5.9	4.00 ± 0.14	90.1 ± 6.0

Model description

The laminar burning velocity for several oxy-mixture composition has been calculated by means of simulation of the one-dimensional, planar, adiabatic, steady, un-stretched, laminar flame propagation, using the PREMIX module of the CHEMKIN package (Reaction Design, v.10) coupled to the detailed Davis reaction scheme [17]. The code, which adopts a hybrid time-integration/Newton-iteration technique to solve the steady-state mass, species, and energy conservation equations, was set up to simulate a freely propagating flame with mixture-averaged formulas. At the inlet boundary, pressure (1 bar), temperature (300 K), and composition of the fresh mixture were assigned. At the exit boundary, all gradients were imposed to vanish.

In the computations, first order windward differences were used for convective terms and second order central differences for diffusion terms. The model uses a non-uniform grid that is successively and automatically adapted based on solution gradients determined on an initially coarse grid.

Most of the scientific studies on syngas combustion have regarded the reaction of fuel with air, starting from Yetter et al. [17], which first elaborated a reaction scheme for syngas/air combustion, developing a detailed kinetic mechanism that has been the basis of several studies and further improvement. Among them, the mechanism of Davis et al. [18], which consists of 14 species and 30 reactions, has been judged the most suitable for the analysis of syngas combustion [19].

Results

Table 1 reports the experimental values of the laminar burning velocity. As expected, the CO_2 addition significantly reduces the laminar burning velocity up to flame extinguishment ($\text{CO}_2 \sim 60\%$; $S_L \sim 5$ cm/s).

We have investigated the nature of the role of CO_2 by *ad hoc* simulations, i.e., by suppressing the kinetics of CO_2 without varying its thermodynamic properties in the Davis mechanism (Figure 2). It appears that the kinetic effects are relevant for high CO_2 concentrations only. This result confirms previous results by the same authors [7,12], which have demonstrated that the main role played by CO_2 is thermal, as the CO_2 addition decreases the flame temperature.

Figure 3 shows the pressure history obtained for some tests reported in Table 1. When enriching the syngas/ $\text{O}_2/\text{N}_2/\text{CO}_2$ mixture with oxygen, the pressure trend is qualitatively different. The pressure time history also shows a pressure peak (~ 100 bar), which exceeds the adiabatic pressure. The occurrence of this anomalous behavior is clear in Table 1 and was named “combustion-induced Rapid Phase Transition” (c-RPT) by the current authors [8-11]. The c-RPT has been demonstrated to be the result of cycles of condensation and vaporization (at the vessel walls) of the water produced by combustion, which culminate into a vapor explosion when the water reaches the super-heating temperature (~ 450 K).

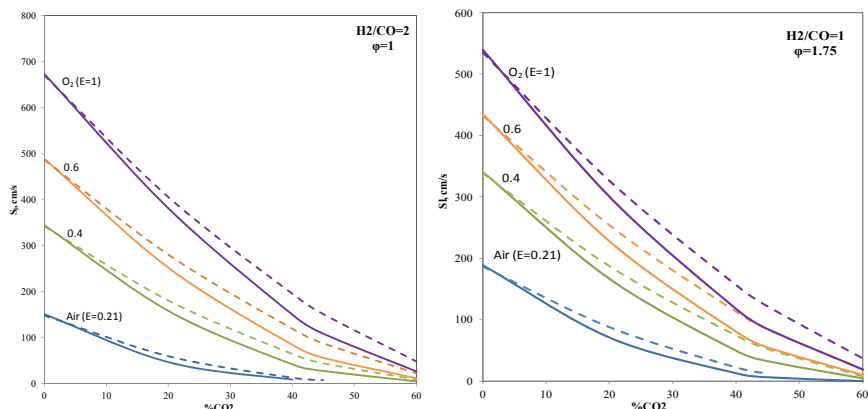


Figure 2. Laminar burning velocity, S_L , versus CO_2 concentration for different oxygen-enrichment factors and equivalence ratios. The dashed lines represent the calculated values obtained using a reactivity-inert species in the place of CO_2 .

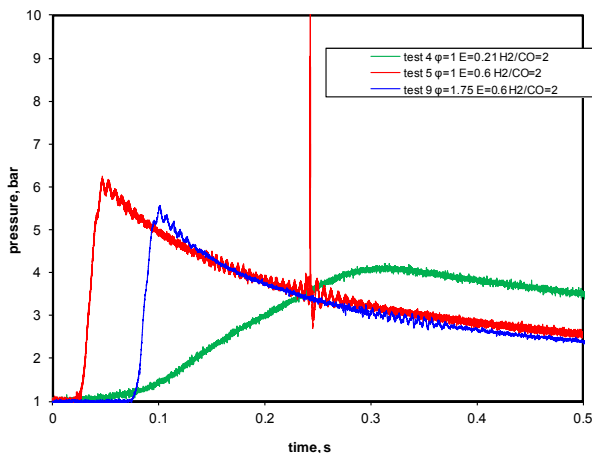


Figure 3. Pressure time histories measured for Tests 4,5 and 9.

Conclusions

The effects of H_2/CO ratio, oxygen-enrichment factor, equivalence ratio and CO_2 content on the laminar burning velocity of syngas/ CO_2 mixtures have been quantified, both experimentally and numerically. The nature of the CO_2 has been found to be mainly thermal, and both thermal and kinetic at low values of the laminar burning velocity.

An anomalous behavior has been found for some oxygen-enriched mixtures due to the occurrence of the c-RPT phenomenon. Future work will be devoted to the evaluation of the c-RPT in syngas mixtures for other syngas compositions.

Acknowledgment

The authors gratefully acknowledge the financial funding provided by Ministero per lo Sviluppo Economico (MiSE) within the project “Carbone pulito”.

References

- [1] Tan, Y., Douglas, M.A., Thambimuthu, K.V., “ CO_2 capture using oxygen enhanced combustion strategies for natural gas power plants”, *Fuel*. 81: 1007–1016 (2002).
- [2] Buhre, B.J.P., Elliott, L.K., Sheng, C.D., Gupta R.P., Wall, T.F., “Oxy-fuel combustion technology for coal-fired power generation”, *Prog Energy Combust Sci*. 31: 283- (2005).
- [3] Dennis, R., *The Gas Turbine Handbook*, National Energy Technology Laboratory, US Department of Energy, 2006.
- [4] Ditaranto, M., Hals, J., “Combustion instabilities in sudden expansion oxy-fuel flames”, *Combust Flame*. 146: 493–512 (2006).
- [5] Lieuwen, T.C., Yang, V., Yetter, R., *Synthesis Gas Combustion: Fundamentals and Applications*, CRC Press, Taylor & Francis, 2010.

- [6] Arpenteiner, P., Cavani, F., Trifirò, F., *The Technology of Catalytic Oxidations. Safety Aspects*, Vol. 2, Ed. Technip: Paris, 2001.
- [7] Di Benedetto, A., Di Sarli, V., Salzano, E., Cammarota, F., Russo, G. "Explosion behavior of $\text{CH}_4/\text{O}_2/\text{N}_2/\text{CO}_2$ and $\text{H}_2/\text{O}_2/\text{N}_2/\text{CO}_2$ mixtures", *Int J Hydrogen Energ.* 34: 6970–6978 (2009).
- [8] Di Benedetto, A., Cammarota, F., Di Sarli, V., Salzano, E., Russo, G., "Anomalous behaviour during explosions of $\text{CH}_4/\text{O}_2/\text{N}_2/\text{CO}_2$ mixtures", *Comb. Flame.* 158: 2214–2219 (2011).
- [9] Di Benedetto, A., Cammarota, F., Di Sarli, V., Salzano, E., Russo, G., "Effect of diluents on rapid phase transition of water induced by combustion", *AIChE J.* 58, 2810–2819 (2012).
- [10] Di Benedetto, A., Cammarota, F., Di Sarli, V., Salzano, E., Russo G., 2012, "Reconsidering the flammability diagram for $\text{CH}_4/\text{O}_2/\text{N}_2$ and $\text{CH}_4/\text{O}_2/\text{CO}_2$ mixtures in light of combustion-induced Rapid Phase Transition", *Chem Eng Sci.* 84: 142–147 (2012).
- [11] Di Benedetto, A., Cammarota, F., Di Sarli, V., Salzano, E., Russo, G., "Combustion-Induced Rapid Phase Transition (cRPT) in $\text{CH}_4/\text{CO}_2/\text{O}_2$ -enriched mixtures, *Energ Fuel.* 26: 4799–4803 (2002).
- [12] Salzano, E., Basco, A., Cammarota, F., Di Sarli, V., Di Benedetto, A., "Explosions of Syngas/ CO_2 Mixtures in Oxygen-Enriched Air", *Ind Eng Chem Res.* 51: 7671–7678 (2012).
- [13] GASEQ, A Chemical Equilibrium Program for Windows. Available at: <http://www.c.morley.dsl.pipex.com>, 2012.
- [14] Dahoe, A.E., De Goey, L.P.H., "On the determination of the laminar burning velocity from closed vessel gas explosions", *J. Loss Prev. Process Ind.* 16: 457–478 (2003).
- [15] Dahoe, A.E., "Laminar burning velocities of hydrogen-air mixtures from closed vessel gas explosions", *J. Loss Prev. Process Ind.* 18: 152–166 (2005).
- [16] Huang, Z., Zhang, Y., Zeng, K., Liu, B., Wang, Q., Jiang, D. "Measurements of laminar burning velocities for natural gas-hydrogen-air mixtures", *Combust. Flame.* 146: 302–311 (2006).
- [17] Yetter, R. A., Dryer, F. L., Rabitz, H. "A comprehensive reaction mechanism for carbon monoxide/hydrogen/oxygen kinetics", *Comb Sci Technol.* 79: 97–128 (1991).
- [18] Davis, S. G., Joshi, A. V., Wang, H., Egolfopoulos, F. "An optimized kinetic model of H_2/CO combustion", *Proc. Combust. Inst.* 30: 1283–1292 (2005).
- [19] Natarajan, J., Lieuwen, T., Seitzman, J., "Laminar flame speeds of H_2/CO mixtures: Effect of CO_2 dilution, preheat temperature, and pressure", *Combust. Flame.* 151, 104– (2007).