



The Effect of Hydrogen addition on the Explosion of Ethanol/Air Mixtures

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The use of hydrocarbon-hydrogen mixtures has been proven to be a valuable system for emission reduction and flame stabilisation. For the assessment of process hazards and the safe design of process equipment handling ethanol-hydrogen, the knowledge of safety parameters, such as maximum pressure, maximum rate of pressure rise and burning velocity, is required.

In this work, the explosion behaviour of pure ethanol and ethanol-hydrogen/air mixtures is studied for different initial temperature and equivalence ratio. Experimental tests are carried out in a 5 dm³ closed cylindrical vessel.

1. Introduction

Ethanol is an important bio-fuel (Turner et al., 2007). It can be produced from agricultural feed-stocks, from forestry wood wastes and agricultural residues. The addition of hydrogen has been also proved to be useful for hybrid fuel mixtures (Di Benedetto et al., 2009). Indeed, hydrogen-enrichment has been proposed as a useful method to overcome drawbacks (local flame extinction, combustion instabilities, lower power output, etc.). However, safe industrial use of this fuel needs explosion data as maximum pressure, maximum rate of pressure rise and burning velocity, which are the most important safety parameters for the assessment of process hazards and the safe design of process equipment.

This work aims at studying the explosion behaviour of pure ethanol and ethanol/hydrogen in air at different initial temperature and equivalence ratio.

To this end, experimental tests were carried out in closed cylindrical vessel. Results were compared with literature data for pure ethanol/air explosion whereas, to the author's knowledge, no ethanol/hydrogen tests with respect to the temperature have been reported in the literature.

2. Experimental

The experimental setup consists of a cylindrical chamber, with volume of 5 dm³ (Figure 1). The initial temperature of the fuel mixture within the chamber is obtained by external heater. The temperature is checked by a thermocouple type K installed in the centre of the chamber. Once the set temperature has been reached, the system is vacuumed. Hence, a small amount of liquid ethanol, which was previously introduced in the sample drum connected to the main chamber under nitrogen atmosphere, is aspirated into the main reactor. Once the system reaches the vapour pressure equilibrium, the system is depressurized to the wished partial pressure. Finally hydrogen, when needed, and air are added up to the atmosphere.

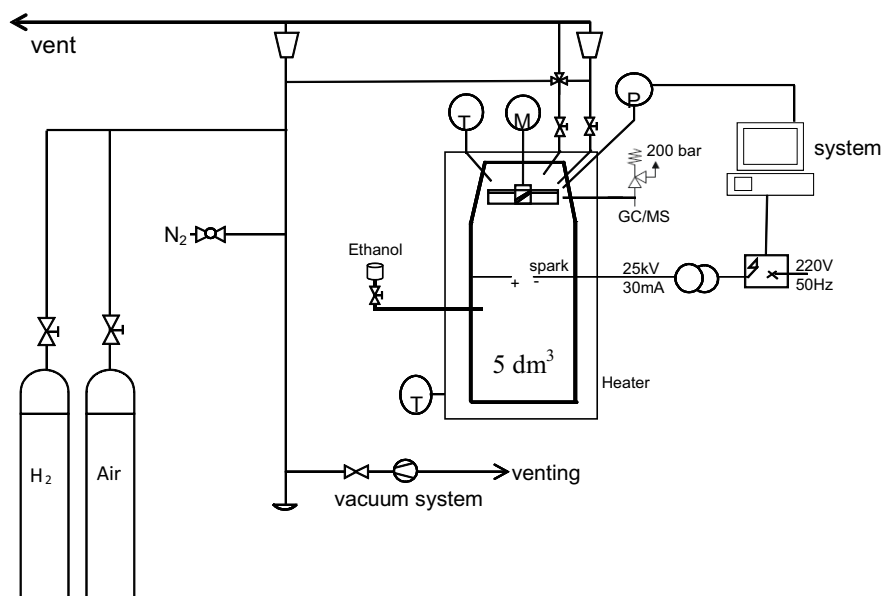


Figure 1: Equipment adopted for the experimental tests.

Explosion tests have been performed at different initial temperatures below and above the boiling temperature of ethanol ($T_{eb} = 351.2$ K), at stoichiometric conditions of fuel (ethanol plus hydrogen) with the air.

In Table 1 the mixture composition analyzed in this work is given, together with the adiabatic pressure P_{ad} as calculated by GASEQ code (GASEQ, 2005) for the given temperature. The parameters λ and X_{FUEL} represent respectively the molar ratio of ethanol over hydrogen and the fuel (ethanol plus hydrogen) molar ratio of the explosive mixture with air. It is worth saying that in all tests the molar fraction of ethanol has been set to 0.065, which is the partial pressure of ethanol at ambient temperature (290 K). Initial pressure is 1 bar.

Table 1: Experimental conditions and mixtures characterization.

T (K)	λ [$H_2/(H_2+EtOH)$]	$H_2/EtOH$	X_{FUEL}	ϕ	P_{ad} (bar)
290	0.000	0.00	0.065	1.00	9.49
360	0.000	0.00	0.065	1.00	7.89
473	0.000	0.00	0.065	1.00	6.11
290	0.393	0.70	0.102	1.15	9.42
360	0.393	0.70	0.102	1.15	7.95
473	0.393	0.70	0.102	1.15	6.16

An electrical transformer (KSEP model 320 primary 220-230 V and 50 Hz, secondary 25 kV 30mA) has been used for spark ignition. Spark gap is about 1 mm. A measure of spark duration gives a time of about 0.01 s. As cited above, mixture composition has been obtained by partial pressure method, starting from vacuum conditions. Stirring of the mixture is produced just few seconds before ignition in order to produce homogeneous mixtures.

Each composition/temperature system has been tested at least two times and the average value was taken. Pressure history has been measured by means of Kulite transducers model ETS-1A-375 series M. Spark, temperature and pressure signals are monitored, controlled and recorded by computerised ultra-fast Digital Acquisition System (National Instrument NI USB-6251), $1.25 \cdot 10^6$ sample s^{-1} .

In order to capture the intrinsic reactivity of ethanol mixtures, the laminar burning velocity has been obtained from time pressure records of explosions occurring in closed vessels, as firstly suggested (Lewis and Von Elbe, 1934). In the present paper, we have calculated the laminar burning velocity from the pressure time history by using the time derivative of flame radius, r_f , as given by the correlation (Dahoe and De Goey, 2003):

$$r_f = \left(\frac{3V}{4\pi} \right) \left[1 - \left(\frac{P^0}{P} \right)^{\frac{1}{\gamma}} \left(\frac{P_{max} - P}{P_{max} - P^0} \right) \right] \quad (1)$$

where γ is the heat capacity ratio, V is the volume, P^0 the initial pressure. The (un-stretched) laminar burning velocity, S_l , was then calculated according to:

$$S_l = \lim_{r_f \rightarrow r^0} \left[\frac{d}{dt} r(t) \right]_{\Delta r_f} \quad (2)$$

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 boundaries of this range were evaluated by considering the places where the time derivative of radius is always positive with radius:

$$\frac{d}{dr} \left(\frac{dr}{dt} \right)_{\Delta r_f} \geq 0 \quad (3)$$

3. Results

The pressure histories of pure ethanol and ethanol/hydrogen mixture for the three analyzed temperatures are shown in Figures 2-3, where the typical trend of explosion in cylindrical vessel may be observed.

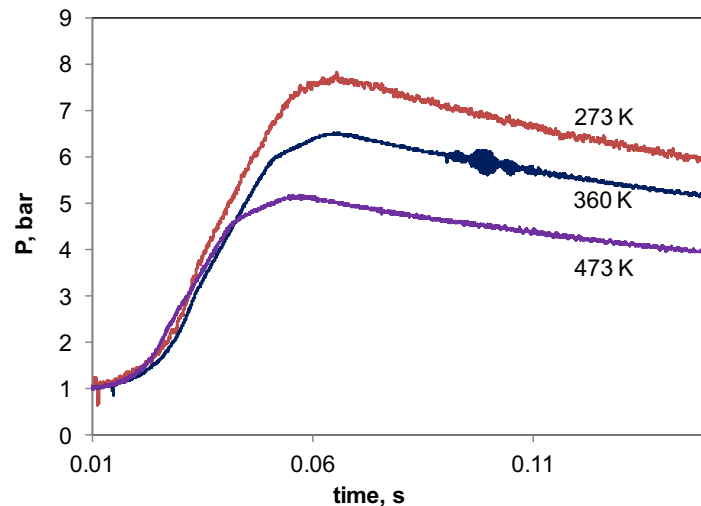


Figure 2: Pressure history for the explosion of pure ethanol in air. $P_{EtOH} = 0.065$ bar.

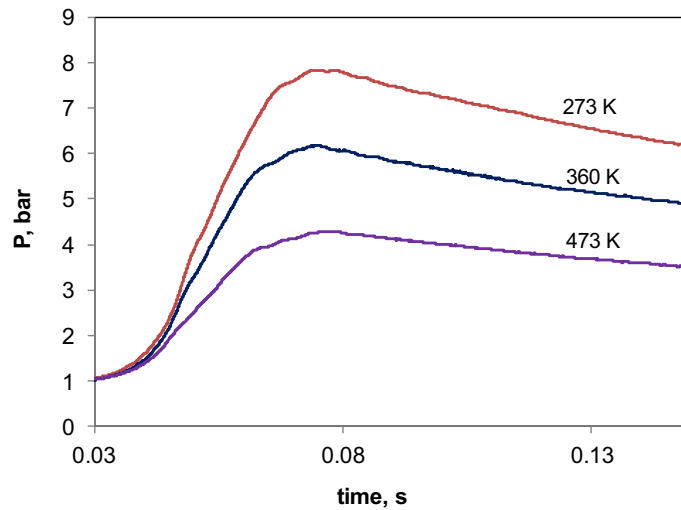


Figure 3: Pressure history for the explosion of ethanol/hydrogen mixtures in air. $P_{EtOH} = 0.065$ bar.

Table 2 reports the obtained experimental maximum pressure and the maximum rate of pressure rise for the mixture compositions and initial temperature reported in Table 1. In Table 2, lower values of experimental value with respect to the adiabatic pressure reported in Table 1 are observed, as expected, due to the non-adiabaticity of the system, i.e. on heat transfer to the steel wall.

The increase of temperature at values either slightly above or consistently higher than the boiling temperature results in the decrease of maximum pressure, due to simple thermodynamic considerations, and in visible diminution of maximum rate of pressure rise, in particular for tests with hydrogen.

For the same compositions, the laminar burning velocities calculated by using Eq. 3), either for pure ethanol or for ethanol/hydrogen mixtures, are reported in the Table 3, by varying the initial temperature.

Table 2: Maximum pressure (P_{max}), maximum rate of pressure rise $(dP/dt)_{max}$ obtained experimentally by varying the initial temperature and hydrogen content for the mixtures of Table 1.

T (°C)	λ	ϕ	P_{ad} (bar)	P_{max} (bar)	$(dP/dt)_{max}$ (bar/s)
290	0.00	1.00	9.49	7.73 ± 0.03	329.3 ± 7.4
360	0.00	1.00	7.89	6.60 ± 0.14	196.9 ± 5.6
473	0.00	1.00	6.11	5.13 ± 0.03	165.2 ± 1.7
290	0.39	1.15	9.42	7.38 ± 0.06	283.6 ± 20.0
360	0.39	1.15	7.95	6.20 ± 0.33	145.8 ± 9.9
473	0.39	1.15	6.16	4.33 ± 0.07	93.4 ± 3.8

Gulder (1982) investigated laminar flame in a constant volume bomb for a wide range of initial pressures, temperatures and equivalence ratios 0.7–1.4. For the tests at 1 bar, the pure ethanol-air laminar flame speed was about 45 cm/sec for $\phi = 1$, which is slightly higher than our values reported in Table 3. More recently, Konnov (2011), reported a lower value, which is in close agreement with our results. Still for pure ethanol in air, both Bradley (2009) and Konnov (2011) at 360 K and Gulder (1982), for the data at 473 K, resulted in experimental values close to our data, despite different techniques – e.g. heat flux method in the case of (Konnov, 2011), hence demonstrating the validity of the methodologies for the evaluation of laminar burning velocity.

Table 3: Laminar burning velocity S_u calculated by using Eq. 3).

T (K)	λ	φ	S_u (m/s)	Other experiments
290	0.00	1.00	0.414 ± 0.064	0.45 (Gulder, 1982); 0.40 (Konnov, 2011)
360	0.00	1.00	0.538 ± 0.001	0.54 (Bradley et al., 2009); 0.53 (Konnov, 2011)
473	0.00	1.00	0.833 ± 0.040	~ 0.90 (Gulder, 1982)
290	0.39	1.15	0.432 ± 0.001	No data available in the literature
360	0.39	1.15	0.667 ± 0.114	No data available in the literature
473	0.39	1.15	0.906 ± 0.025	No data available in the literature

4. Discussion

The classical correlation for temperature, equivalence ratio dependence of laminar burning velocity has been tested for the mixtures analyzed in this work:

$$S_u(T, \varphi) = S_u^o(T^o, \varphi) \cdot \left(\frac{T}{T^o} \right)^n \quad (4)$$

where the S_u^o refers to the laminar burning velocity at ambient conditions T^o . To the aim of evaluating the value of exponent n in Eq. 4), we adopted a best fit method for the dependence of laminar burning velocity of pure ethanol and ethanol/hydrogen mixtures with air by varying the initial temperature (Figure 4). The value for the pure ethanol gives an exponential coefficient n of 1.5, whereas that for ethanol/hydrogen is slightly lower, about 1.4. This small variation let us to say that the effect of hydrogen addition does not change dramatically the temperature dependence of laminar burning velocity, at least in the analyzed range.

It is worth saying that a value of n of about 1.7 for pure ethanol was found by Gulder (1982), and more recently by Liao et al. (2007) and Bradley et al. (2009). On the other hand, Konnov (2011) has found a value of 1.47 base on more refined experimental and numerical methodologies. It should be also noted that most of these authors limited the analysis to temperatures lower than 400 K, with the exception of (Liao et al., 2007). No study was found in the open literature for ethanol/hydrogen mixtures with air.

5. Conclusions

Preliminary results have showed the behaviour of ethanol/air and ethanol/hydrogen/air mixtures with temperature and equivalence ratio by adopting a closed vessel, explosion system. In particular, this method has been used for the definition of the effects of hydrogen addition on pure ethanol/air at different temperature, by comparing the laminar burning velocity calculated through the pressure history measured in the equipment. This method, although with some uncertainties with respect to more refined methodologies, allow the easy possibility of working at any pressure and temperature. The obtained data allow further advancements on safety for the use of hybrid fuels containing hydrogen.

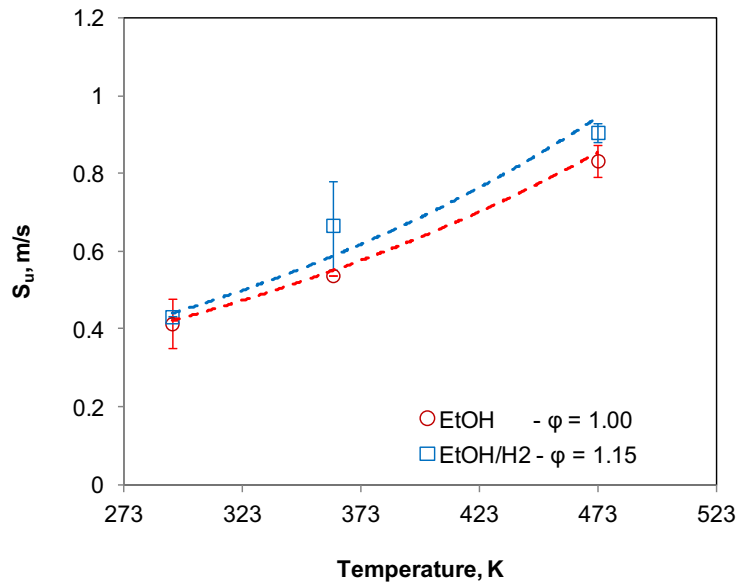


Figure 4: Burning velocity with respect to temperature for the analysed equivalence ratio.

Acknowledgment

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References

- Bradley D., Lawes M., Mansour M.S., 2009, Explosion bomb measurements of ethanol–air laminar gaseous flame characteristics at pressures up to 1.4 MPa, *Combustion and Flame*, 156, 462–1470.
- Dahoe A.E.; De Goeij L. P.H., 2003, On the determination of the laminar burning velocity from closed vessel gas explosions, *Journal of Loss Prevention in the Process Industry*, 16, 457-478.
- Di Benedetto A., Di Sarli V., Salzano E., Cammarota F, Russo G., 2009, Explosion behavior of CH₄/O₂/N₂/CO₂ and H₂/O₂/N₂/CO₂ mixtures, *International Journal of Hydrogen Energy*, 34, 6970-6978.
- GASEQ, 2005, A Chemical Equilibrium Program for Windows. <www.c.morley.dsl.pipex.com>, Accessed 08/05/2012.
- Gulder O. L., 1982, Laminar Burning Velocities of Methanol, Ethanol and Isooctane-Air Mixtures, 19th Symp. (International) on Combustion, The Combustion Institute, Naples, Italy, 275-281.
- Konnov A.A., Meuwissen R.J., de Goeij L.P.H., 2011, The temperature dependence of the laminar burning velocity of ethanol flames, *Proceedings of the Combustion Institute*, 33, 1011–1019.
- Lewis B., Von Elbe G., 1961. *Combustion, flames and explosions of gases*, II Ed. Academic Press: New York, United States.
- Liao S.Y., Jiang D.M., Huang Z.H., Zeng K., Cheng Q., 2007, Determination of the laminar burning velocities for mixtures of ethanol and air at elevated temperatures, *Applied Thermal Engineering*, 27, 374–380.
- Turner J.W.G. Pearson R.J. Holland B.P.R., 2007, Alcohol-based fuels in high performance engines, SAE Paper 2007-01-0056.