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Ignition energy and flame propagation in ethylene oxide- air mixtures

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Abstract

Although Ethylene oxide (EO) is a root product in the industry, its flammable properties are not very well known because they are difficult to measure partly because this product is very dangerous but also because the Minimum Ignition Energy is said to be very small.

The aim of this work is to provide accurate experimental data about the minimum ignition energies, the flammable limits and burning properties of ethylene oxide air mixtures at ambient conditions.

To do this a very specific device including a new type of spark generator was developed and calibrated against known mixtures (propane, hydrogen). The explosion chamber is a 7 litre transparent and closed explosion cylinder so that flame velocities and pressure effects could be obtained.

Systematic measurements were performed for EO-air mixtures varying the EO concentrations from 4 to 22% v/v. The minimum ignition energy is 40 μ J for 10% EO in air at ambient conditions. This is lower than found in the literature. The burning velocity could be estimated and is about 1.6 m/s. Two reaction regimes were identified. Below about 13% a standard burning is observed (blue flame) producing CO₂ and consuming O₂. Above this value, a bright flame is seen producing smoke without any oxygen consumption nor CO, CO₂, H₂ formation suggesting a polymerization.

Keywords: *ethylene oxide, minimum ignition energy, flame speed, explosion severity*

1. Introduction

Ethylene oxide (EO) is not a new product (widely used at a raw base in the chemical industry) but its flammable properties look strange (upper flammable limit up to 100% v/v....) and seem difficult to obtain because of the significant toxicity of the product (Bonnard et al., 2006) but also because of the Minimum Ignition Energy (MIE) might be very small.

The aim of this work is to provide accurate experimental data about the minimum ignition energies, flammable limits of ethylene oxide air mixtures and burning properties.

In the following, the experimental device designed and operated for this purpose is described including safety consideration in the first section. In the second section the experimental results are presented.

2. Experiments

2.1 Ethylene oxide risk profile

EO is very difficult to handle because toxic, unstable (Bonnard et al., 2006)... Three exothermal reaction regimes were identified producing a propagating front. In dense phase, ethylene oxide may self-polymerise which may occur when exposed to a fire. But in vapour phase, pure ethylene oxide may decompose into carbon, methane and hydrogen (theoretical estimation) under the form of a cool

flame propagating rather slowly. It can be triggered by an intense spark (tens of mJ). Mixed with air, ethylene oxide burns as a traditional fuel. The estimated MIE would be obtained for rich mixtures (10% v/v) and the maximum laminar burning velocity would be on the order of 1.08 m/s. The upper flammability limit is obviously 100% v/v. The lower flammability limit is about 3% v/v and the stoichiometry is 7.7 % v/v (Brighton, 1990).

Using the flame propagation theory (Glasmann, 1977), a laminar burning velocity of 1 m/s will give a quenching distance, D_{quench} , of about 1 mm (Peclet number=50). Using the well know D_{quench}^2 correlation with MIE (Kuchta, 1985), the minimum ignition energy should be on the order of 50 μJ .

EO is particularly toxic (Bonnard et al., 2006): irritant, carcinomic and mutagen. IDLH¹ (30 mn exposure) is 800 ppm producing oedema, and the carcinogenic and mutagen effects are possible above a few tens of ppm for a chronic exposure. The smell is detectable at 300 ppm.

2.2 Explosion vessel and associated piping

The explosion chamber is a 7-liter transparent cylindrical chamber (Figure 1) able to support a static internal pressure amounting 100 bars. It is equipped with many measuring ports and feeding lines. The supplier provides ethylene oxide under liquid form only conditioned in small (5 l) containers. The mixture is prepared into a stainless-steel mixing tank (4 l) using the partial pressure method (Kistler piezoresistive 0-10 bar gauges) . The first step is to evacuate the mixing tank, then some liquid EO is introduced using a micrometric manual valve. Enough time is provided for the pressure to reach equilibrium and air is introduced until the desired concentration is reached. Then again some time is allowed for the mixture to equilibrate. This procedure and the homogeneity of the mixture are controlled using oxygen meters located on the purge line (Servomex paramagnetic sensor). Dry air only was used. The explosion chamber is carefully dried and evacuated before introducing the mixture inside the explosion chamber. Note that because of the serious hazards associated with EO, a specific experimental design was performed following a detailed risk analysis. One consequence is that the device has to be confined into a box which was purged continuously with the outside air.

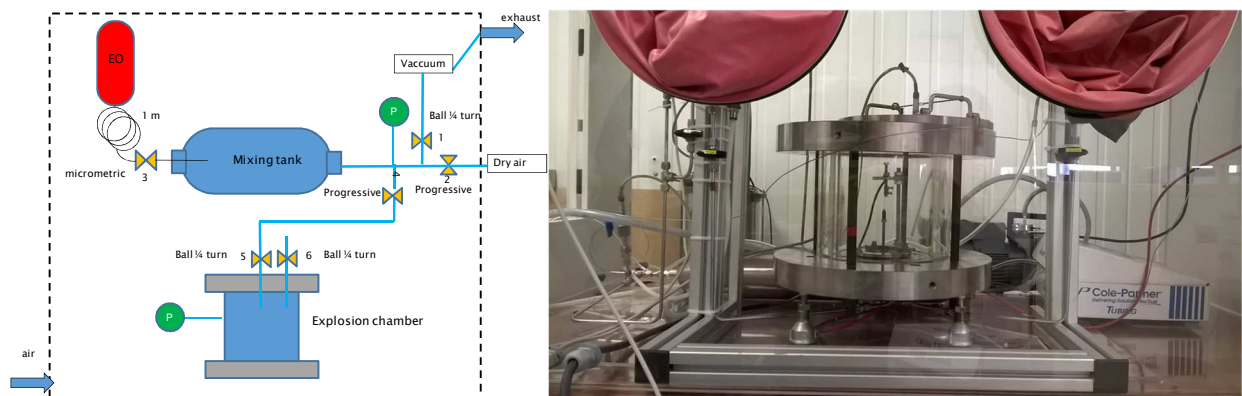


Fig. 1: setup (left) and explosion chamber (right: 200 mm ID and 200 mm high)

2.3 Spark gap generator

A new type of **spark generator** was devised. It is designed to reduce the overlap between ignition and no ignition zones and to better control the energy delivered inside the spark gap. Details are given elsewhere (Proust, 2020). An electrical spark is a two steps process. During the “disruption phase”, a large voltage is required (typically 3000 V/mm) to ionize the atmosphere and create a “streamer”. The current remains very low during that phase (micro amperes). After, the “arc” starts during which a large current flow through the spark gap. During this second phase, the voltage amounts some tens of volts with currents amounting some Amperes. In the present spark generator, it was decided to disconnect the two phases of the spark. A separate high voltage and high impedance circuit is used to produce the streamer (Figure 2). A second, low voltage and low impedance circuit, is used to produce

¹ Immediately Dangerous to Life or Health

the arc and dissipate the energy. The high voltage current is delivered through a set of 7 resistors (1 G Ω each) limiting the current supplied by the generator to about 1 μ A. The low voltage current is delivered to the charge capacitor through a set of 11 resistors (1 M Ω each) offering the possibility to produce continuous sparking at a rate of about 10-100 Hz. A 1 mH coil is in series to limit the current through the spark (thus decreasing Joule losses). A Zener diode prevents the high voltage to be transmitted to the low voltage circuit. The contactor is on the high voltage circuit. Once the streamer is created the low voltage circuit discharges automatically. The current is measured using a standard current gauge (Wide Band Current Transformers STANGENES 2-0.1W) and the voltage with a high voltage probe (Tektronics P6015A). The electrodes are in tungsten, 0.3 mm in diameter, with rounded extremities, with a spark gap of 0.5 mm.

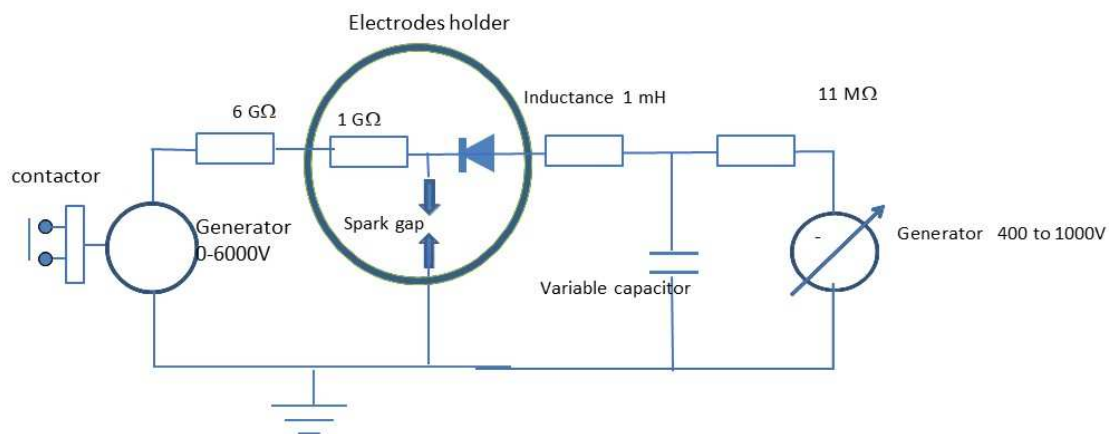


Fig. 2: scheme of the electrical circuit

The spark gap and the Zener diodes being short circuited, the total capacitance of the low voltage part of the circuit is that of the charge capacitor. A residual value of 5-10 pF is constituted by the high voltage probe. If no coil is added, the inductance is 1.7 μ H and the resistance is 0.1 Ω . With the coil inserted, the inductance is 1 mH and the resistance is 2 Ω . Because of the high voltage required to trigger the arc, any capacitance on the high voltage side of the circuit may store and add a significant amount of energy to the spark under the form of a tiny precursor spark. It was measured that a 1 m high voltage cable amounts about 20 pF which is much too large (energy stored = 90 μ J...). To remove this difficulty an extra resistor is added at the closest to the spark gap, on the electrode holder. Observations revealed that very tiny sparks occurred even when the low voltage circuit was not charged. This means that a residual capacitance remained. The high voltage circuit and the Zener diode are responsible for this. It was found that the residual capacitance of the high voltage circuit is only 1 pF and that of the diode is 3 pF so, 4 pF in total. It was verified that these precursor sparks are not able to ignite any mixtures (even H₂-air). The energy delivered by the precursor spark was added up to that of the low voltage capacitance. Further testing was performed to investigate the low voltage part behavior. The current and the voltage were measured at the spark gap (Figure 3). The very beginning of the current signal is an artifact probably due to the Zener diodes closing the low voltage part of the circuit. The signals resemble that of a typical RLC circuit and can be modelled rather faithfully. Such modelling can be used to estimate the yield of the spark (ratio of the electrical energy consumed in the spark gap divided by that stored in the low voltage capacitor). In the situation of Figure 8, with a reduced current, the yield is about 90%. In most situation the yield was about 70%.

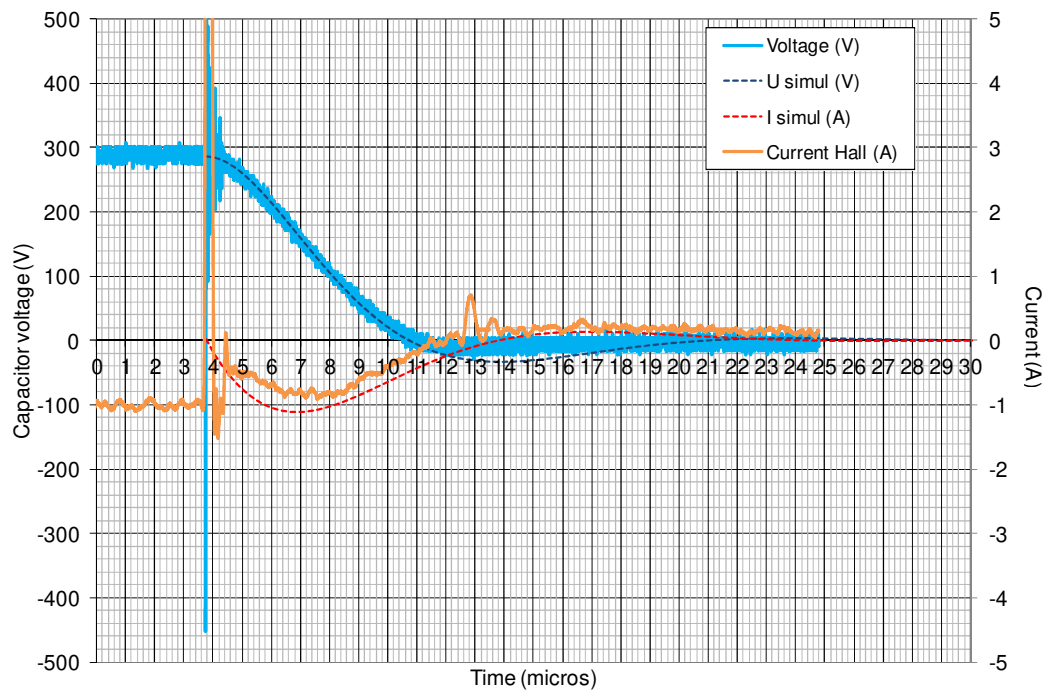


Fig. 3: current voltage signals: streamer triggered spark, with a 1 mH additional inductance, 290 V in the 20 nF capacitor, with the diodes.

2.4 Measurements

The maximum explosion (over)pressures is measured using a Kistler 10 b piezoresistive gauge. High speed video (up to 10000 fps: Photron camera) is used.

Normally, the ignition diagnostic is straightforward (flame propagation and pressure increase) but may be more difficult for slowly reactive mixtures (near the flammability limits for instance). In such a case, the final diagnostic rests on the behavior of the initial flame kernel. If it grows linearly with time, ignition is successful otherwise it shrinks. But even if some flame kernel growth is detected and ignition is physically achieved, in some situations, the flame ball could be convected upwards and ultimately be quenched in contact with the cold upper flange of the chamber, thus not providing any explosion. This is more likely for very small chambers and may not occur with the present experimental configuration.

The energy delivered by the spark is obtained by measuring the voltage of the arcing circuit (low voltage capacitor). The yield is depending on this and was measured while developing the spark generator. The energy delivered to the spark gap is that stored in the low voltage capacitor plus that stored by the high voltage part of the circuit times the yield.

2.5 Calibration

The **MIE measurement** method was designed and checked at ambient temperature using reference fuels propane and hydrogen since the expected MIE for EO is supposed to lie between that for those reference fuels. As experimentalists know, the ignition threshold may differ when starting from the no ignition zone and increasing gradually the spark energy until ignition than when starting from a positive ignition point and decreasing the energy. MIEs are much higher with the former procedure. The reason is unclear but perhaps the combustion “cleans up” or chemically activates the tip of the electrodes. In the following, the ignition threshold was looked for using the second procedure (starting for a positive ignition and decreasing the energy). To vary the ignition energy, the value of the capacitor was adapted (100 pF to 5000 pF) and the voltage was varied (between 400 and 1000 V). The energies on the following graphs are that stored in the low voltage capacitor and in the streamer

high voltage capacitors (4 pF). To calculate the latter the breakdown voltage was measured by decreasing the high voltage until no spark occurred anymore (2700 V with the air of the bottle at ambient temperature and atmospheric pressure). Results obtained at room temperature are presented on figure 4. Note that each point represents at least 1 second of continuous sparking, so typically 50 sparks. The values are in line with the data from the literature (Randeberg and Eckhoff, 2007; Ono et al., 2007) with a minimum at 20% amounting 18 μJ for hydrogen air mixtures and about 300 μJ for stoichiometric propane air mixtures.

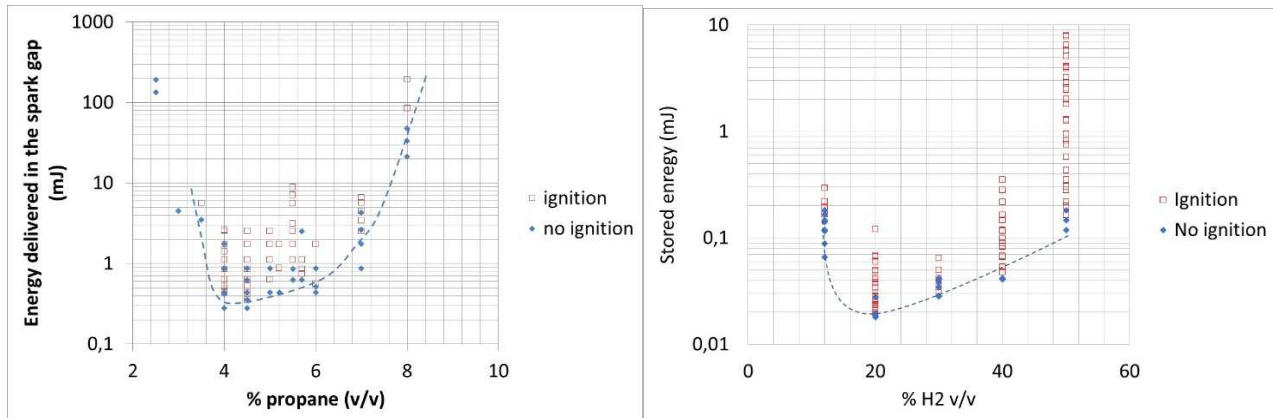


Fig. 4: Measured MIEs for C_3H_8 air (left) and for H_2 -air mixtures at ambient conditions (right)

3. Results and discussion

3.1 Ignitability and flammability

The measurement of MIE for EO-air mixtures at ambient conditions are presented on Figure 5

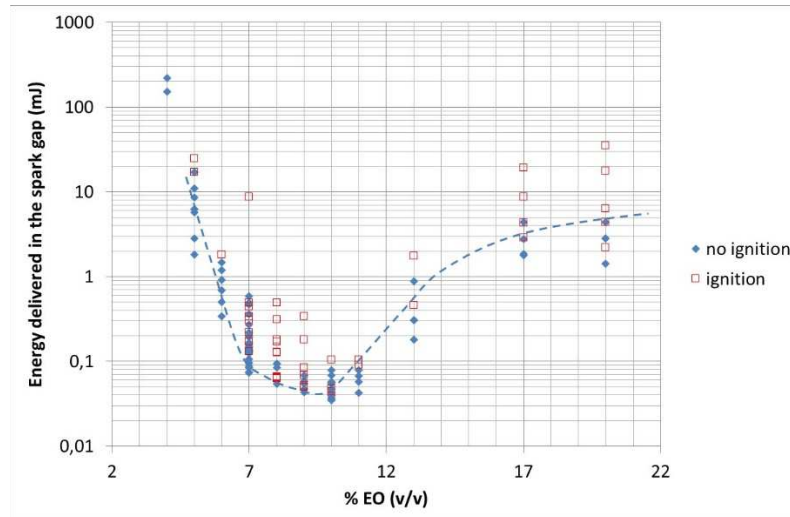


Fig. 5: measured minimum ignition energies for ethylene oxide air mixtures at ambient conditions

The minimum ignition energy is about 40 μJ and is obtained for 10% v/v EO in air in reasonable agreement with expectations. A change in the traditional U shape curve is noticed above 13% v/v EO in air suggesting a change in the chemical mechanism. This point is addressed later.

The lower flammability limit might be close to 4%v/v EO in air. There is not sign of upper limit but rather some plateau in the ignition energy (10 mJ) suggesting a different kind of propagation.

3.2 Explosion and flame propagation

A typical sequence of photos is shown on Figure 6 for the flame propagating a 7% v/v EO-air mixture. The pictures were postprocessed to increase the contrast and ease the calculation of the outwards flame velocity. In the present case, the outwards velocity, V_f , around the ignition point is 3 m/s (less than 10 cm from the ignition point).

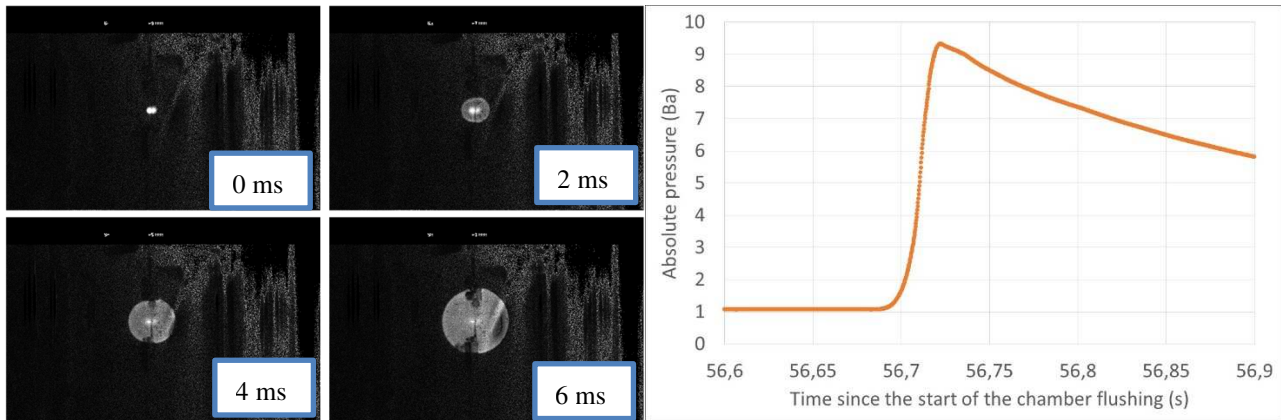


Fig. 6: flame kernel development (7% EO, 2 ms between frames) and pressure time trace

Explosion parameters are shown in Table 1 below. The explosion severity index K_G was derived from the maximum explosion pressure rise (dP/dt_{max}) and the vessel volume (V) using the “cubic law” recalled in expression [1] (Mittal, 2017). The expansion ratio (Exp) of the burned products was deduced from the maximum explosion pressure (P_{vmax}) using expression [2] (from Proust, 2017). The laminar burning velocity Sl is simply the ratio between the outwards flame velocity divided by the expansion ratio. Maximum explosion pressures and outward flame velocities are given in Table 1.

$$K_G = \left(\frac{dP}{dt} \right)_{max} \cdot V^{1/3} \quad [1]$$

$$Exp \approx \frac{1}{\gamma_p} \cdot \left(\frac{P_{vmax}}{P_{init}} - 1 \right) \quad [2]$$

where P_{init} is the initial pressure and is the ratio of specific heats of the burnt product (typically 1.35).

The burning velocity at 10% is about =1.5 m/s. This is on the order of values for lean hydrogen air mixtures for which the minimum ignition energy might range between 20 and 100 μ J. Consequently, the measured minimum ignition energy for EO-air mixtures seems logical. Note the laminar burning velocity is hardly varying as function of the EO concentration which is an unusual behavior and would need clarification.

Table 1: explosion parameters for EO-air explosion (ambient initial conditions): accuracy of % EO $\pm 0.1\%$ v/v, of P_{max} $\pm 0.01b$ and of V_f $\pm 0.1m/s$

% EO v/v	P_{vmax} (ba)	$(dP/dt)_{max}$ (b/s)	Kg (b.m/s)	Vf (m/s)	Exp	SI (m/s)
5	6,5	125	24	6,5	4,07	1,60
6	7,9	280	54	7,9	5,11	1,55
8	9,3	750	143	9,3	6,15	1,51
9	9	810	156	9	5,93	1,52
10	9,4	980	187	9,4	6,22	1,51
11	9,5	1000	191	9,5	6,30	1,51
13	9,2	650	124	9,2	6,07	1,51
17	8,6	330	63	8,6	5,63	1,53
20	8,4	200	38	8,4	5,48	1,53

3.2 Burning mechanisms ?

Perhaps the rather strange behavior of flame propagation in EO-air mixtures has to do with the flame chemistry. As said before there is a turning point in the MIE curve at 13% v/v EO in air. Pictures of the flame are presented on Figure 7. Below 11% the flame is blue, at 17% it is shallow green and bright orange above. 13% is intermediate between blue and green. The strong evolution of the luminosity suggests a significant change in the chemistry.

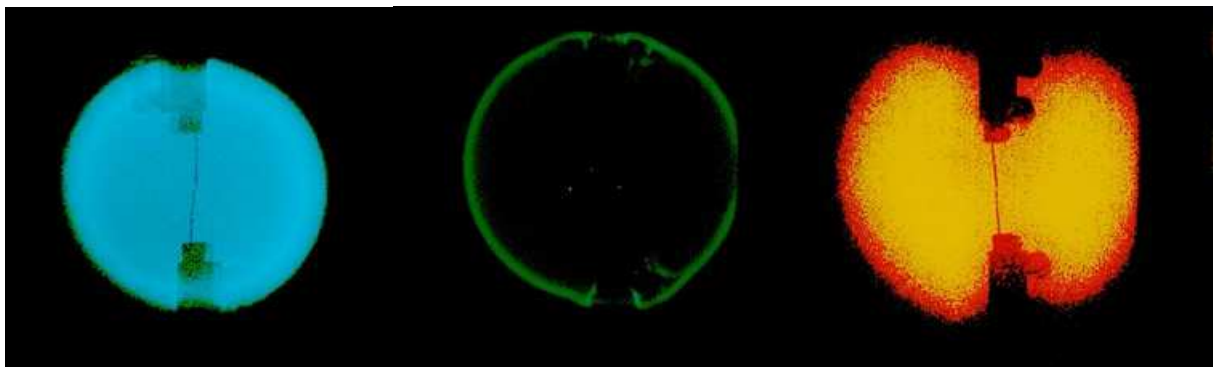


Fig. 7: pictures of EO-flames at 5 cm from the ignition point (left 11% v/v EO, center 17 % and right 20%)

To start investigating this aspect the burnt gases were sampled and analyzed using gas chromatography. The results are shown in table 2. Water is condensed to perform the measurements. For the 7% EO-air mixture a classical combustion occurs producing CO_2 (and certainly water). For the rich mixture (20% EO v/v), there is no combustion (no CO, CO_2 no O_2 consumption) but a lot of smoke and dust into the vessel suggesting a polymerization of the ethylene oxide.

Table 2 : gas chromatography of the burned gases for EO-air explosion (ambient initial conditions)

Gas	7% EO	20% EO
H ₂	< 10 ppm	< 10 ppm
O ₂	11.1±0.4 %	20.0±0.7 %
N ₂	81.1±7 %	76.0±6.7 %
CO ₂	6.86±0.47 %	0.16±0.02 %
CO	86±14 ppm	0.51±0.04 %
CH ₄	< 25 ppm	46±5 ppm

4. Conclusions

A new generation of spark generator was developed to measure very low minimum ignition energies (MIE). The performances of the device were checked by comparing the measured MIEs for propane air mixtures with various compositions and of for a H₂-air mixtures.

Systematic measurements were performed for EO-air mixtures varying the EO concentrations from 4 to 22% v/v. The minimum ignition energy is 40 µJ for 10% EO in air at ambient conditions. The burning velocity could be estimated and is about 1.5 m/s and KG amounts nearly 200 b.m/s.

Two reaction regimes were identified. Below about 13% a standard burning is observed (blue flame) producing CO₂ and consuming O₂. Above this value a bright flame is seen producing smoke without any oxygen consumption nor CO, CO₂, H₂ formation suggesting a polymerization.

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