On the experimental determination of the minimum ignition energy for α-pinene/air mixtures

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1   Introduction

Volatile Organic Compounds (VOCs) emissions in the atmosphere have anthropogenic and biogenic origins. At earth scale, the natural sources represent a great part of the total VOCs emissions but in industrialized regions, the anthropogenic emissions become majority due to the various human activities (fuel evaporation, industries, solvent use…). α-Pinene is a volatile organic compound widely found in air freshener, home fragrance and household products and also emitted by several vegetal species. Its annual North American biogenic emission rate can reach up to 4.5 Mt which rank it as the second emitted VOC after isoprene [1]. It has been shown recently by Chetehouna et al. [2] that the α-pinene ($C_{10}H_{16}$) is the main constituent emitted by *Rosmarinus officinalis* shrubs heated by means of a radiant panel in a hermetic enclosure. More recently, Zhao et al. [3] found also that this VOC is the major compound emitted from heated *Pinus pumilia* needles and twigs. Courty et al. [4] highlight the fact that the experimental lower flammability limits of α-pinene at various temperatures do not exceed 1%. Renane et al. [5] computed laminar burning speeds at different temperatures using FDS code and shown that this volatile organic compound has high values. All those works point out that there is a high risk related to α-pinene substance which must be taken into account to prevent ignition hazards in industrial process and forests. In addition to the lower flammability limit, the minimum ignition energy (MIE) is a useful parameter to predict this ignition hazards. To our knowledge, this flammability characteristic has never been determined for α-pinene.

The aim of this paper is to investigate the minimum ignition energy for α-pinene/air mixtures at a given temperature and for different equivalence ratios. Several studies [6-8] on the MIE are based on a capacitive spark discharge but this kind of apparatus is highly influenced by the circuitry and electrode geometry. Unlike this conventional ignition system, devices based on the use of laser ignition source offer more advantages which are a better control of the timing and location of ignition and also the non-intrusive nature. See the review of Phuoc [9] for more details.

In this work, the measurement of the minimum ignition energy for α-pinene/air mixtures are performed using a laser-induced spark ignition experimental system previously developed [10]. The next section is devoted to the presentation of the experimental apparatus and procedures used to

determine the minimum ignition energy of α-pinene. The third section is dedicated to the results and discussions.

2   Experimental devices and procedures

The laser beam is provided at 1064 nm by a Q-switched Nd:YAG laser (Quantel Brilliant). The Gaussian beam (quality factor $M^2 = 1.95$, diameter d = 6 mm) is focused in the center of the combustion chamber by a 150 mm focal length lens. As the pulse duration equals 4.48 ns, a high irradiance is provided. As a result, multi-photon ionization and the subsequent electronic avalanche occur. These processes are at the origin of the non-resonant laser breakdown phenomenon.

The incident energy E_{inc} and the energy absorbed by the laser spark E_{abs} are monitored by two Ophir Nova energy meters coupled with 10-AP thermal sensors. E_{abs} is obtained from the incident energy E_{inc} measured at the output of the laser and the energy measured after the combustion chamber, taking into account the absorption of the windows, see [10] for more details. A photodiode detector is used to monitor the laser spark emission.
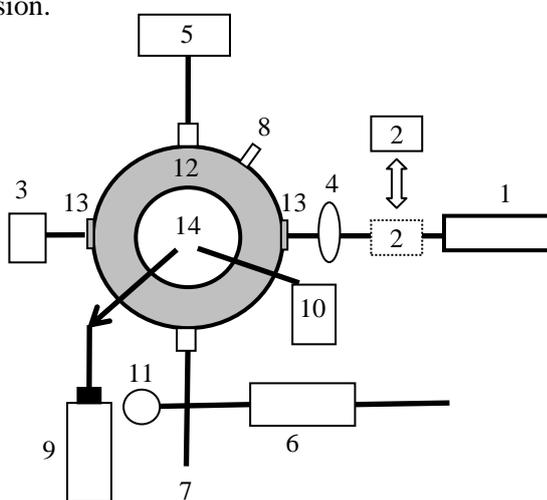
Figure 1: Sketch of the experimental apparatus (1) Nd:YAG laser (2) mobile energy meter (3) fixed energy meter (4) 150 mm focal length lens (5) pressure transducer (6) vacuum pump (7) gas inlet (8) septum (9) camera (10) photodiode detector (11) manometer (12) combustion chamber (13) antireflection-coated window (14) quartz window.

The combustion chamber is cylindrical (l = 200 mm, D = 80 mm) with a volume of 1L. It is fitted with two quartz windows in order to visualize the laser spark and the combustion process. They are orthogonal to two anti-reflection coated BK7 windows (d = 15 mm) allowing the passage of the laser beam. The reactive mixture is obtained from synthetic air (80% N_2, 20 % O_2, CO_2 <1 ppm, CO 1 ppm, H_2O < 3 ppm, C_nH_m<0.1 ppm), and from liquid α-pinene with a degree of purity of 98 %. The mixture preparation follows the partial pressures method. The chamber is first placed under vacuum. Then the liquid fuel is directly injected into the combustion chamber through a septum using a micrometric syringe. Synthetic air is then admitted with a flow rate of approximately 2 L/min. The combustion chamber and the gas feeding pipe are heated at T = 347 K to allow the fuel vaporization over a wide range of fuel equivalence ratio. The chamber is filled with synthetic air and placed under vacuum twice between each reactive experiment in order eliminate residual products of combustion and moisture. The walls of the chamber are periodically cleaned. A Cormak 9555 differential manometer with one mbar accuracy is used for the static pressure measurements. During combustion experiments, the pressure evolution is monitored by a piezoelectric transducer (Kistler 603B) with a charge amplifier (Kistler 5011).

3   Ignition probability and energy absorption

In the presented work we worked with 5 equivalence ratio Φ (0.9, 1.1, 1.3, 1.5 and 1.7) and 3 incident energies (33, 35 and 37 mJ) for equivalent ratio from 0.9 to 1.3 and 2 incidents energies (33 and 35 mJ) for the lasts equivalent ratio. For each couple equivalent ratio Φ and incident energy fifty shots were done, so results presented here are based on 650 experiments. The table 1 presents the breakdown probability with a 2% uncertainties α-pinene/air mixture at a pressure P equal to 1 bar and a temperature T equal to 347 K for the five equivalent ratio Φ and the 3 incident energies coming from the laser source. Figure 2 shows the extrapolation of the breakdown probability coming from the table 1 assuming in a first approach a linear extrapolation of the obtained values.

Table 1: Breakdown probability in % versus incident energy for the 5 equivalent ratio Φ.

Equivalent ratio Φ	Incident energy [mJ]		
	33	35	37
0,9	6	10	56
1,1	2	16	54
1,3	8	18	62
1,5	6	38	
1,7	6	46	
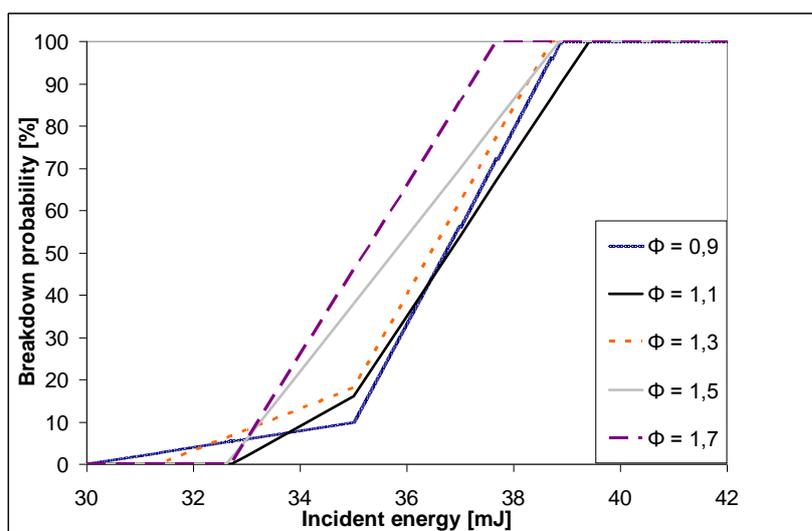
Figure 2. Breakdown probability versus incident energy.

From the measured data and its extrapolation it appears that the breakdown probability of the studied mixture rise a lot in a short range of incident energy compared to acetone air mixture [10] for example. However a breakdown doesn't necessary lead to an ignition of the mixture because the energy absorbed by plasma may be too low to cause ignition. Moreover, according to Tihay et al. [10] it is more appropriate to express the ignition probability in function of the energy absorbed by the plasma than the incident energy. So, in figure 3, the ignition probability is given in as a function of the absorbed energy. One can note that for all equivalent ratios the absorbed energy needed to ignite the mixture is low. Moreover let us pinpoint that for all equivalent ratios, except 0.9, the ignition probability is upper than 60% for an energy absorbed equal to 2 mJ, which is a low value.
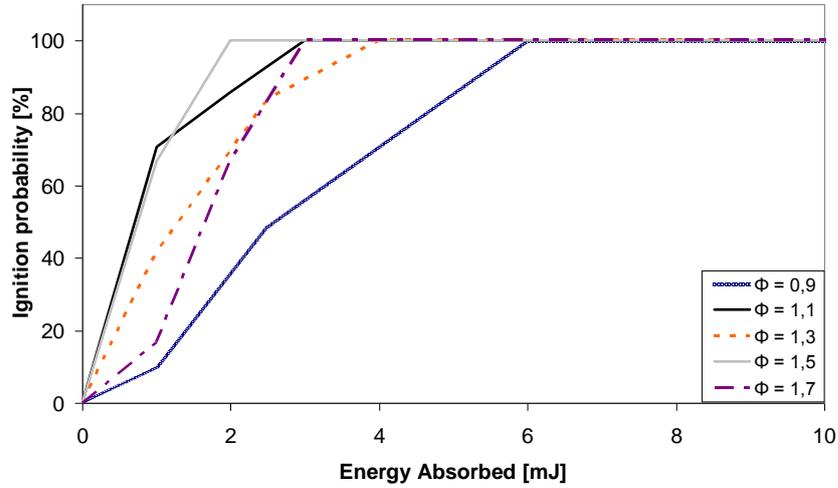
Figure 3. Ignition probability versus the energy absorbed by the plasma.

This low level of energy is also well illustrated with the Minimum Ignition Energy (MIE) diagram depicted in figure 4 and values given in table 2.

Table 2: Minimum Ignition Energy for the 5 equivalent ratio Φ.

Equivalent ratio Φ	MIE [mJ]
0,9	1,33
1,1	0,51
1,3	0,43
1,5	1,10
1,7	1,23
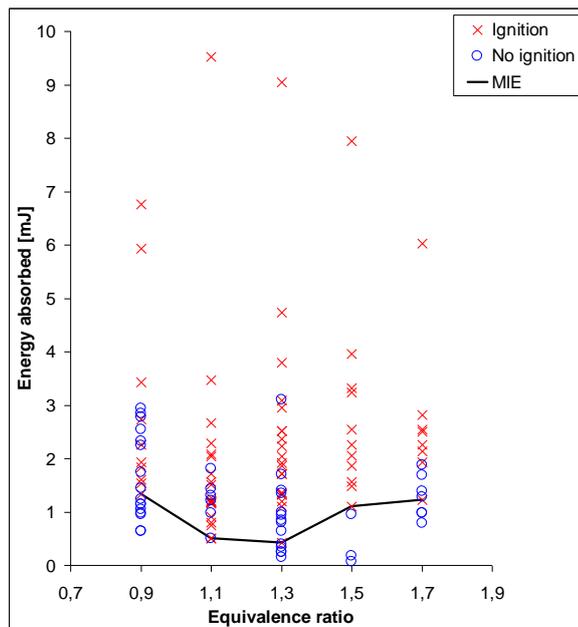
Figure 4. Ignition probability versus the energy absorbed by the plasma.

As we can see in the figure 4 the MIE for all equivalence ration of the α-pinene/air mixture is under 2 mJ and its minimum is for the equivalent ratio 1.3. This MIE is in the same range than the one of a propane/air mixture [11-12] However the MIE represents the lower energy absorbed for the ignition, as a consequence this point is also the lowest point of the ignition probability. In order to have a larger view about the hazard of the α-pinene/air mixture the figure 5 presents on a diagram containing equivalence ratio and energy absorbed three zones: no ignition, transition zone and systematic ignition. The no ignition and systematic ignition zones represent respectively the 0% and 100% ignition probability while the transition zone represents the range 0 to 100% ignition probability. The boundary between no ignition and transition zone is the MIE and the boundary between the transition zone and the systematic ignition is the 100% probability of ignition. This figure highlights that the transition zone is narrow compared to other mixture such as acetone/air [10], and at the equivalent ratio 1.5 it is the shortest which means that the ignition probability is more sensitive to the amount of energy absorbed when it is above the MIE than for other equivalent ratio.
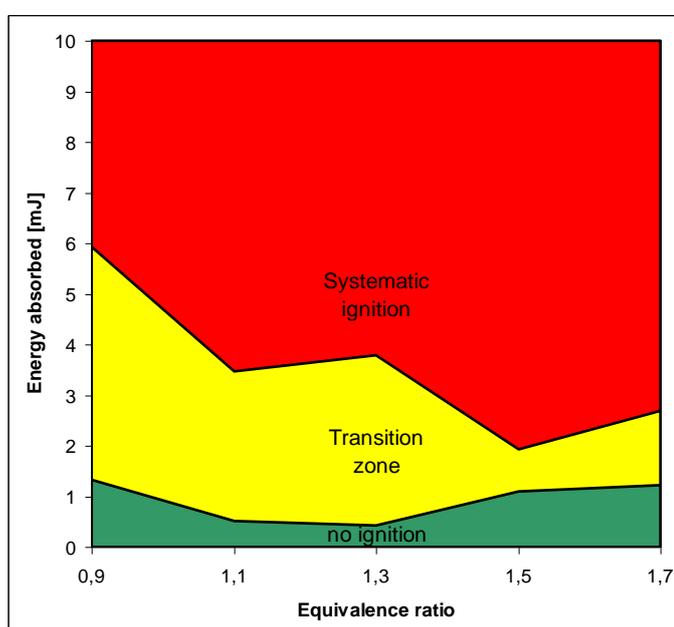
Figure 5. Ignition probability versus the energy absorbed by the plasma.

4   Conclusion

This work is the first attempt to determine the MIE of the α-pinene/air mixture using a laser-induced spark ignition. It points out the particularities of this widely used mixture in industries. The first noticeable point is that the breakdown probability quickly rises in a short range of incident energy (from 30 to 39 mJ). Then a quick rise of the ignition probability for low energy absorbed has been pinpointed (the smallest range of energy absorbed for 0 to 100 % ignition probability is 0 to 2 mJ for $\Phi = 1.5$ and the largest one is 0 to 6 mJ for $\Phi = 0.9$). After that the measurements of the MIE has given the lowest value at 0.43 mJ for $\Phi =1.3$ and one can note the all MIE are in a low range of 0.43 to 1.33 mJ. To finish, the last noticeable point is that for all equivalent ratio the transition zone is restrained, especially for $\Phi =1.5$.

To conclude, reminding that α-pinene have a lower flammability limits which not exceed 1% [4], this preliminary experimental work shows the potential threat of the α-pinene/air mixture with MIE measurements. In a future work we plan to study the effect of the temperature on such material.

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