Laminar burning speeds of α-pinene/benzene/air mixtures involved in the combustion in forest fires

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1 Introduction

Forest fires are a growing issue with regards to the physical planning aspect and the preservation of the local territory. Indeed, forest fires are more and more uncontrollable, being the result of abundant undergrowth in some areas. The rural flight and the development of agrochemical gave place to a declining interest of mountain pastures and free-range farming in favor to intensive agriculture into the great plains. Bushes have taken over control the undergrowth and fire outbreaks in these zones are feared for their dangerousness causing unstoppable forest fires. Sometimes these fires are controlled without deaths but in other cases, the fire can be unpredictable and may kill firefighters on the field or civilians. One of these unpredictable behavior is called accelerating forest fire (AFF) or eruptive fire. An AFF is characterized by an augmentation of the rate of spread and of the energy released by the fire so it can be almost regarded as a flashover if we focus on the visual aspect. The reasons which bring to this phenomenon are not very well understood even if we know that it occurs in very particular conditions. Therefore, AFFs reported in the literature always happen in summer during particular dry seasons and in typical topographies like thalwegs and canyons [1,2]. The phenomenon reaches principally the Mediterranean countries in lands covered by aromatic plant species which releases a strong odor before these AFFs [3]. Another noteworthy particularity is that this kind of fires does not accelerate just after the starting fire but always spend at least one hour before accelerating. All these parameters lead to the main hypothesis based on a thermochemical approach. This thermochemical approach supports that Volatile Organic Compounds (VOCs) coming from smokes and heated vegetation are able to create a flammable atmosphere near the fire front, especially in recirculation zones where heavy compounds can easily accumulate. Some authors already demonstrated that the Mediterranean vegetation like Pinus pinea, Rosmarinus officinalis, Lavandula stœchas, Cistus albidus and Thymus vulgaris emits much more when exposed to high temperatures than in normal conditions of temperature [4-6]. Regarding these works which study biogenic VOC emissions, α -pinene (C₁₀H₁₆) and its isomers were found to be the main compounds emitted among Mediterranean plant species. As regards the forest fire smokes, several studies have been done during a forest fire to analyze the smokes and the principal VOC appears to be benzene (C_6H_6) [7-9]. It is well known that carbon monoxide and carbon dioxide are predominant in forest fire smokes but VOCs represent heavier

molecules which are more likely to accumulate near the ground around vegetation which is where AFFs are propagating. The fact that α -pinene and benzene have very low values of lower flammability limits, near 1% vol. in air [10] strengthens our hypothesis. There are already some studies on α -pinene and to be closer to the AFF conditions we chose to study mixtures of α -pinene/benzene/air by varying different parameters. An experimental work has already been done on the Minimal Ignition Energy of different proportions of this mixture [11], the present experimental study permits to complete these data but by focusing on laminar burning speed and Markstein length. Varying the fuel proportion, the equivalence ratio and the temperature permits to reproduce the conditions of different starting points of an AFF more or less close to the fire front.

2 Experimental description

Mixtures of α -pinene/benzene/air were investigated in this paper. From our different experiments two different combustion properties were studied, laminar burning speed and Markstein length. Three different parameters were varied, the initial temperature, the equivalence ratio and the fuel proportions. Initial temperature was chosen at 75, 120, 150 and 180 °C. The equivalence ratio was experimented between 0.7 and 1.5 with a step of 0.1. The fuel proportion represents the relative proportion of α pinene and benzene which were chosen respectively at 20%-80%, 50%-50% and 80%-20% to reproduce different conditions of smoke and vegetation before an AFF. As stated in the introduction, in real cases, our three parameters will not be the same whether, where the ignition starts. A spherical chamber of 4.2 L was used for this study, made of four windows providing optical access into the chamber. A vacuum is created before filling the chamber with our mixtures. We control the amount of gases introduced into the chamber is controlled with a thermal mass flow meter to know if the amount of fuel injected is totally vaporized. Synthetic air (79.5% N₂ and 20.5% O₂) was used for the experiments. High purity α -pinene and benzene (> 98% pure from Sigma-Aldrich) were injected through a Coriolis mass flow meter. To produce spark ignition at the center of the chamber, two tungsten electrodes, with a 1 mm gap, are connected to a conventional capacitive discharge ignition system. The measurements were repeated three times for each condition. The relative error on the equivalence ratio is around 2%, and the uncertainty of unstretched laminar burning speed is lower than 5 cm/s. The combustion properties are determined thanks to flame images obtained by shadowgraphy by using a parallel light created with a lamp and two plano-convex lenses (25 mm and 1000 mm focal lengths). The shadowgraphic images were recorded using a high speed video CMOS camera (Photron APX) working at 10,000 frames per second with an exposure time of 20 µs. The study consists in analyzing the temporal evolution of the expanding spherical flame. Figure 1 presents a scheme of the experimental setup.

Thanks to the shadowgraphy system, a luminous circle indicates the localization of the instantaneous flame front with burned gases inside the circle and unburned ones outside. The images with flame radii less than 7 mm were not taken into account to determine the laminar burning speed and Markstein length, so as to avoid the effect of the initial spark energy deposit [12-14]. In order to neglect the increase of pressure, flame radii larger than 25 mm were not taken into account. In these conditions, the total volume of burned gases is less than 1.6% of the chamber volume. In the constant-pressure spherical flame method, the stretched premixed flame speed with respect to burned mixture $S_b = \frac{dR_f}{dt}$ and the stretch rate, $\kappa = 2S_b/R_f$, are obtained from the flame front history, $R_f = R_f(t)$, recorded by high-speed shadowgraph photography. The values of the laminar burning speeds S_u^0 are calculated from the relation linking them to the unstretched laminar flame speeds, S_b^0 , by means of the expansion factor, σ , $S_u^0 = \sigma \cdot S_b^0$. The unstretched laminar flame speed, S_b^0 , and Markstein length, L_b , with respect to burned mixture are extracted based on an extrapolation model used in the data processing of the spherical flame method; this is a nonlinear model [15-16]. Because of the complexity of the mixture it is difficult to find a suitable expansion factor. Moreover, there are few works in the literature dealing with VOC combustion, none about a detailed chemical-kinetic

mechanism for α -pinene combustion, even less about a mixture of our two VOCs. Consequently, we chose to estimate the expansion factor using the adiabatic flame calculation via the combustion reaction of α -pinene with air.



Figure 1. Schematic overview of the emission setup. Right: Scheme of the spherical combustion chamber.

3 Results and discussion

This section presents the laminar burning speeds and Markstein lengths of α -pinene/benzene/air mixtures which have been studied for different proportions of fuels: 80%-20%, 50%-50% and then 20%-80%, percentages representing respectively α -pinene and benzene. Laminar burning speeds of the three proportions are presented in Fig. 2 and 3. One can observe in these two figures that laminar burning speed increases with temperature for each proportion of our two fuels. If we compare the different proportions, one can note that the maximal laminar burning speed is different whether α -pinene or benzene is the main compound of the mixture. When α -pinene is the major compound, the maximum is located for an equivalence ratio of 1.1 like most compounds. When benzene is the major compounds with benzene rings [17].



Figure 2. Laminar burning speeds of α -pinene/benzene/air mixtures (80%-20% at the left side 50%-50% at the right side) at 1 atm as a function of equivalence ratio for different temperatures



Figure 3. Laminar burning speeds of α -pinene/benzene/air (20%-80%) mixtures at 1 atm as a function of equivalence ratio for different temperatures



Figure 4. Laminar Burning Speed at 180°C for different equivalence ratios and fuel mixtures

Figures 4 presents a comparison of S_{α}^{0} at 180°C for different proportions including pure α -pinene from a previous study [18]. 180°C was chosen as the temperature of the maximal VOC emission of Mediterranean plant species like *Thymus vulgaris* et *Lavandula stoechas* [4,5]. First, results are in good agreement with the study of pure α -pinene. Then, the shift of the maximal laminar burning speed can be observed from 1.1 to 1.2 with the increase of benzene percentage in the mixture. It is also noticeable that for rich mixtures, equivalence ratios from 1.1 to 1.5, there is also an increase of the laminar burning speed for the same equivalence ratio with the increase of benzene proportion. These remarks are also valid for the other temperatures.

The following results obtained with the combustion chamber are related to Markstein lengths. Markstein length is a key parameter to characterize premixed flame stability and is deduced from the nonlinear relationship between the flame speed and flame stretch rate. Figures 5 and 6 present the results for 80%-20%, 50%-50% and 20%-80% of α -pinene and benzene proportions. The values of Markstein length are always positive until equivalence ratio of 1.3 for mixtures containing more benzene and 1.4 for mixtures with more α -pinene. Then the stability of the flame depends on the fuel proportions. For 80%-20% of α -pinene and benzene, the flame becomes unstable at equivalence ratios of 1.4 and 1.5. For 20%-80, the flame is unstable only at 1.5. Results of 50%-50% are falling in between. If we compare the Markstein lengths for the different proportions we observe therefore that the presence of benzene seems to stabilize the flame.

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Figure 5. Markstein length as a function of equivalence ratio for α -pinene and benzene proportion of 80%-20% at the left side and 50%-50% at the right side.



Figure 6. Markstein length as a function of equivalence ratio for α -pinene and benzene proportion of 20%-80%

In conclusion, the presence of benzene would have a substantial influence into a gas cloud of α -pinene. With major proportions of benzene, the maximum laminar burning speed is reached for richer mixtures around 1.2 instead of 1.1 and values of speed are higher than for pure α -pinene. The second point is that with high proportions of benzene the flame becomes more stable for rich mixtures.

References

[1] Eruptive Fire Behaviour in Past Fatal Accident. Viegas and Pita (2005)

[2] Viegas et al. (2009). Recent Forest Fire Related Accidents in Europe. Publications Office of the European Union.

[3] Dold J, Simeoni A, Zinoviev A, Weber R. (2009). The Palasca fire, September 2000: Eruption or Flashover ?, Recent forest fire accidents in Europe, Viegas (ed.).

[4] Barboni T, Cannac M, Leoni E, Chiaramonti N. (2011). Emission of biogenic volatile organic compounds involved in eruptive fire, implications for the safety of firefighters, International Journal of Wildland Fire, 20, 152-161,

[5] Chetehouna K, Barboni T, Zarguili I, Leoni E, Simeoni A, and Fernandez-Pello AC. (2009). Investigation on the emission of volatile organic compounds from heated vegetation and their potential to cause an accelerating forest fire. Combust. Sci. Technol., 181, 1273–1288.

[6] Owen SM, Boissard C, Hewitt CN. (2001). Volatile organic compounds (VOCs) emitted from 40 Mediterranean plant species, VOC speciation and extrapolation to habitat scale. Atmospheric Environment, 35, Issue 32, 5393–5409.

[7] Evtyugina M, Calvo AI, Nunes T, Alves C., Fernandes AP, Tarelho L, Vicente A, Pio C. (2013). VOC emissions of smouldering combustion from Mediterranean wildfires in central Portugal, Atmospheric Environment, 64, 339-348.

[8] Statheropoulos M and Karma S. (2007). Complexity and origin of the smoke components as measured near the flame-front of a real forest fire incident: A case study, Analytical and Applied Pyrolysis, 78, 430-437.

[9] Barboni T, Cannac M, Pasqualini V, Simeoni A, Leoni E, Chiaramonti N. (2010). Volatile and semi-volatile organic compounds in smoke exposure of firefighters during prescribed burning in the Mediterranean region, International Journal of Wildland Fire, 19, 606–612.

[10] Catoire L, Naudet V. (2005). Process Safety Progress 24, 130-137.

[11] Coudour B, Chetehouna K, Rudz S, Gillard P, Garo JP. (2015). Investigation on minimum ignition energy of mixtures of α -pinene–benzene/air, Journal of Hazardous Materials, 283, 507–511.

[12] Bradley D, Gaskell PH, and Gu XJ. (1996). Burning velocities, Markstein lengths, and flame quenching for spherical methane-air flames: A computational study. Combust. Flame, 104, 176–198.

[13] Bradley D, Hicks RA, Lawes M, Sheppard CGW, and Woolley R. (1998). The measurement of laminar burning velocities and Markstein numbers for iso-octane–air and iso-octane–n-heptane–air mixtures at elevated temperatures and pressures in an explosion bomb. Combust. Flame, 115, 126–144.

[14] Chen Z, Burke MP, and Ju Y. (2009). Effects of Lewis number and ignition energy on the determination of laminar flame speed using propagating spherical flames. Proc. Combust. Inst., 32, 1253–1260.

[15] Halter F, Tahtouh T, Mounaïm-Rousselle C. (2010). Nonlinear effects of stretch on the flame front propagation. Combustion and Flame, 157, 1825–1832.

[16] Coudour B, Chetehouna K, Courty L, Lemée F, Mounaïm-Rousselle C, Halter F. (2014). Combustion characteristics of two biogenic volatile organic compounds: 1-fenchone and 3-hexen-1-ol. Combust. Sci. Technol., 186: 1–11.

[17] Marshall SP, Taylor S, Stone CR, Davies TJ, Cracknell RF. (2011). Laminar burning velocity measurements of liquid fuels at elevated pressures and temperatures with combustion residuals, Combustion and Flame, 158, 1920-1932.

[18] Courty L, Chetehouna K, Halter F, Foucher F, Garo JP, Mounaïm-Rousselle C. (2012). Experimental determination of emission and laminar burning speeds of α -pinene, Combustion and Flame, 159, 1385-1392.