

ON THE EMISSION AND COMBUSTION CHARACTERISTICS OF LIMONENE INVOLVED IN ACCELERATING FOREST FIRES

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Abstract

Several researches have reported that under certain conditions forest fires with normal behaviour suddenly start to propagate at unusual and very fast rate of spread. Over the last decade, these accelerating forest fires were responsible for many fatalities in Europe. A thermochemical approach, based on the ignition of a Volatile Organic Compounds (VOCs) cloud, has been proposed previously to explain this phenomenon. Indeed, some vegetal species when heated emit volatile substances. We have shown that a typical Mediterranean plant, *Rosmarinus officinalis*, emit fourteen components. One of the main VOCs emitted is limonene. The acceleration of the rate of spread can be the consequence of the ignition of this emitted gas. The measurement of the laminar burning speed and combustion characteristics of limonene/air premixed flames is essential to take into account this approach in forest fire modelling.

Laminar burning velocities and Markstein lengths of limonene/air premixed flames are determined using the spherical expanding flames method. Experiments are carried out in a spherical vessel at atmospheric pressure. The effects of equivalence ratio (0.7 to 1.4) and unburned gas temperature (353 to 453 K) are studied. Unstretched propagation speeds and Markstein lengths are obtained using a nonlinear methodology. A correlation is developed to calculate the laminar burning speeds as a function of equivalence ratio and temperature. The PREMIX code of the CHEMKIN package is used to compute laminar flame velocities with the *San Diego* chemical kinetic mechanism of JP-10, which is an isomer of limonene. The experimental results are compared to the computed ones of JP-10 as well as to those found in the literature for this compound and for n-decane.

Introduction

Several researches have shown that under some conditions forest fires behave in a surprising way [1,2,3], changing suddenly from an ordinary behaviour (moderate rate of spread) to an explosive propagation, characterized by a rate of spread and an energy released much more important. This phenomenon is known as accelerating forest fire for its explosive nature or eruptive fire for the continuous rise of the fire rate of spread. Fires propagating in terrain specific configurations, like canyons, can lead to such fire explosions and are responsible for many fatalities in the past. Indeed, the Sintra and La Gomera accidents occurred respectively in Portugal in 1966 and in Spain in 1984, causing the death of 25 and 20 persons [4]. More recently, in 2007, this phenomenon happened in Greece in Artemida, killing 24 persons [5].

The mechanisms which explain this type of forest fires are not totally well known yet. A thermochemical approach, based on the ignition of a Volatile Organic Compounds (VOCs)

cloud, has been proposed [6]. According to these authors, the acceleration of the rate of spread can be the consequence of the ignition of the VOCs emitted by fire heated vegetation and accumulated in canyons. Indeed, some vegetal species of the Mediterranean basin produce and emit volatile substances when they are heated [7,8]. In this study, we will show that the monoterpene hydrocarbon ($C_{10}H_{16}$) limonene is one of the major components emitted by a *Rosmarinus Officinalis* plant when heated by a radiant panel simulating the fire front. Courty et al. [9] have measured the lower flammability limits of α -pinene and limonene and determined their standard enthalpies of formation at 298.15 K in the gas phase. Recently, they determined the combustion characteristics of α -pinene [10].

Forest fires propagation models do not take into account until now the possible ignition of a VOCs cloud accumulated in a canyon. An accurate modelling of such phenomenon requires measurements of the combustion characteristics of these VOCs. Knowing these parameters, it will be possible to predict the accelerating forest fires accidents with the existing propagation models [11,12].

In this paper, we focus on the characterisation of the VOCs emission of a heated *Rosmarinus Officinalis* plant and on the determination of the combustion characteristics of limonene. To proceed, adapted experimental methodologies for the emissions and combustion measurements are chosen. The experimental setups, results and discussions are presented in the following sections.

Volatile Organic Compounds emissions in an emission chamber

In this work, a batch of 33 *Rosmarinus officinalis* plants was used to determine the effects of plant temperature on the emission of VOCs. These plants were placed in an emission chamber and were heated by a radiant panel. The emission chamber, with the dimensions of 100 cm \times 100 cm \times 134 cm, is designed in cellular-concrete material with a thickness of 7 cm and its volume is 1.2 m³. The radiant panel is constituted of 16 black ceramics plates of a 144 cm² surface, providing a maximal thermal power of 19.2 kW. The experimental setup is presented in Figure 1.



Figure 1. Pictures of the VOCs emissions experimental setup.

The average mass, height and moisture content of the *Rosmarinus officinalis* plants were respectively 155 g, 30 cm and 70 %. They were placed at the centre of the hermetic enclosure, 50 cm from the radiant panel, and heated during 30 min. The heat flux of the radiant panel

was varied from 0.44 to 20.59 kW · m⁻². The experimental protocol consisted in trapping and sampling the VOCs with glass multibed tubes, to transfer them into a freezing box to the chemistry laboratory and to analyse them with an ATD-GC/MS instrument. Each experiment was performed in triplicate.

The aim of these experiments was to study the VOCs emission as a function of temperature in order to estimate the VOCs quantity emitted by the vegetation during a forest fire. The selected temperature range was between 303 and 483 K to simulate the heating of plants by a fire front before the pyrolysis phase. This range of temperature corresponds to the radiant panel heat flux range indicated above. The sampling height and time were respectively 112 cm and 10 min. A gas mixture containing 14 compounds is identified and presented in Table 1.

Table 1. Identification of the VOCs emitted by a *Rosmarinus Officinalis* shrub.

N°	VOCs
1	α -Pinene
2	Limonene
3	Camphene
4	Filifolone
5	β -Pinene
6	Myrcene
7	<i>p</i> -Cymene
8	Thuja-2.4-(10)-diene
9	Verbenone
10	Terpinolene
11	Sabinene
12	α -terpinene
13	γ -terpinene
14	Camphor

This mixture is characterized by high contents of monoterpenes hydrocarbons (C₁₀H₁₆). Indeed, the main components were α -pinene, limonene, camphene, myrcene and β -pinene. The same compounds were observed in [13] for emissions of *Rosmarinus officinalis* under natural conditions. Figure 2 illustrates the evolution of limonene and total VOCs emissions as functions of the plant temperature.

It was noticed from this figure that the VOCs emissions increase with the plant temperature until 448 K. The same tendency was observed in [14] for other Mediterranean tree species such as leaves of *Pinus nigra* and *Pinus pinaster*. The VOCs mixture amount at 448 K is 8 times higher than the one measured around 323 K. Moreover, we can see an increase of VOCs production around 393 K due to the transport of the VOCs by the

evaporation process. Knowing that the boiling temperature of monoterpenes is about 427 K, these molecules would be in a liquid or in a vapour-liquid equilibrium state below this temperature. As a consequence, for the temperatures higher than this value, the VOCs emission increases rapidly to a maximum at 448 K. In this temperature range, the total emission of the VOCs is about 4 times more important than in the range 323 – 393 K. After 448 K, we can observe a significant decrease of the VOCs amount that can be explained by the thermal degradation of the terpene molecules.

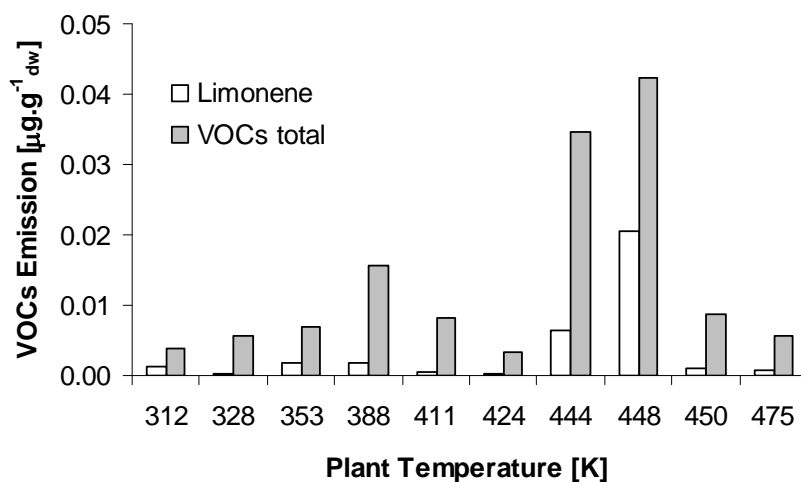


Figure 2. Limonene and total VOCs emission as functions of temperature.

Laminar burning speeds and Markstein lengths of limonene

Experimental setup and methodology

The combustion characteristics measurements were made using a stainless steel spherical combustion chamber. Four windows provided optical access into the chamber. Before filling the chamber, vacuum was first created. The amount of gases introduced into the chamber was controlled with a thermal mass flow meter. High purity limonene was injected through a Coriolis mass flow meter. The temperatures chosen to study the effect of temperature on the combustion characteristics were 353, 373, 398, 423 and 453 K. This range of temperatures is the one given in Figure 2. The equivalence ratio values were varied between 0.7 and 1.4 with a 0.1 step. Two tungsten electrodes were used to produce spark ignition at the centre of the chamber. For each condition, the measurements were repeated three times.

The flame images were obtained by shadowgraphy. The temporal evolution of the expanding spherical flame was then analysed. A detailed description of the experimental protocol is given in [15]. Figure 3 illustrates some examples of flame front propagation. The luminous circle is an image of the instantaneous flame front: burned gases are inside the circle and unburned ones outside. The images with flame radii less than 7 mm were not analyzed to determine the laminar premixed flame parameters, so as to avoid the effect of the initial spark energy deposit [16,17]. During the initial stage of flame expansion, the total chamber pressure was constant, so flame radii larger than 25 mm were not taken into account, corresponding to a total volume of burned gases less than 1.6 % of the chamber volume.

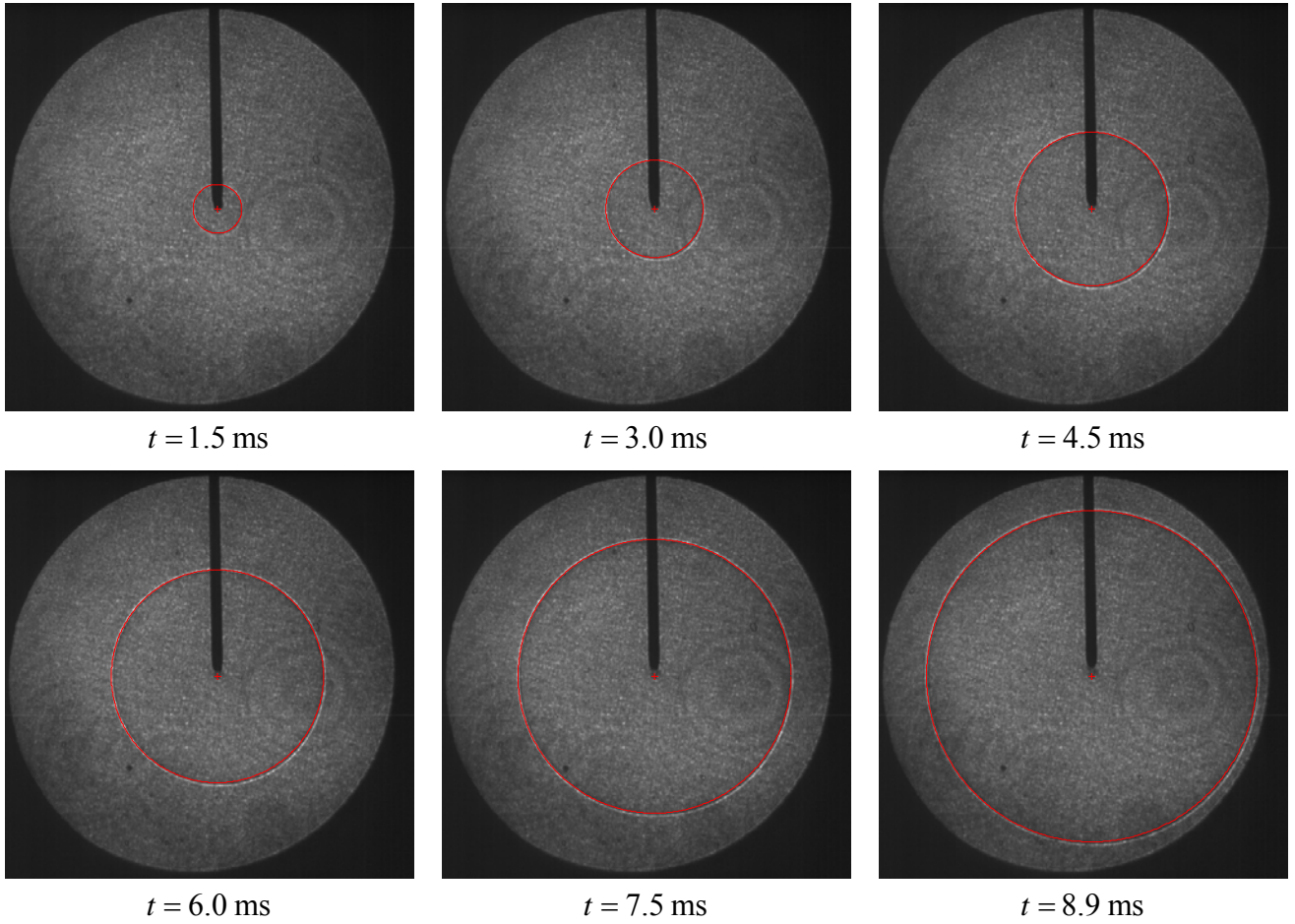


Figure 3. Temporal evolution of the flame front of a stoichiometric limonene/air mixture ($T = 453 \text{ K}$, 10000 images/s).

The stretch influences propagation, stability and structure of the premixed flames and affects the determination of their speeds. Under the hypotheses of low stretch values (i.e. for flame radii larger than their thicknesses) and high activation energies, it has been shown that the stretched premixed flame speeds was linked to the stretch by the following relation [18]:

$$\bar{s}_b^2 \ln(\bar{s}_b^2) = -2 \frac{L_b}{s_b^0} \kappa \quad (1)$$

where $\bar{s}_b = \frac{s_b}{s_b^0}$ is the normalized unstretched flame speed, s_b^0 is the unstretched flame speed, L_b is the Markstein length and κ is the flame stretch.

If we replace $s_b = \frac{dR_f}{dt}$ in equation (1) and if we integrate it, the analytical solution of the flame radius can be given by the following expression:

$$\begin{cases} t = \frac{2L_b}{s_b^0} \left[E_1(\ln \eta^2) - \frac{1}{\eta^2 \ln \eta} \right] + C \\ R_f = -\frac{2L_b}{\eta \ln \eta} \end{cases} \quad (2)$$

where $E_1(\eta) = \int_{\eta}^{\infty} \frac{e^{-x}}{x} dx$ is the exponential integral function, $\eta \in [e^{-1}, 1]$ for $L_b > 0$, $\eta \in [1, \infty[$ for $L_b < 0$ and C is an integration constant.

The unstretched premixed flame speed s_b^0 can be determined from equation (1) using the temporal evolutions of the stretched premixed flame speeds obtained with experimental flame radii derivation and with the analytical solution of equation (2). The identification process of this parameter can then be shared into two steps. The first one consists in minimizing the following objective function:

$$J_1(\xi) = \left\| \left(\frac{dR_f^{\text{exp}}(t)}{dt} \right)^2 \ln \left[\frac{1}{\xi_1^2} \left(\frac{dR_f^{\text{exp}}(t)}{dt} \right)^2 \right] + 2\xi_1\xi_2\kappa \right\| \quad (3)$$

where $\xi = (\xi_1, \xi_2) = (s_b^0, L_b)$ is the vector of parameters to determine, $R_f^{\text{exp}}(t)$ is the experimental flame radius and $\|\cdot\|$ is the usual Euclidian norm. These optimization results will be used as initial parameters for another optimization based on the analytical flame radius. The objective function to minimize can therefore be written:

$$J_2(\tilde{\xi}) = \left\| \left(\frac{dR_f^{\text{th}}(t, \xi_1, \xi_2, \xi_3)}{dt} \right)^2 \ln \left[\frac{1}{\xi_1^2} \left(\frac{dR_f^{\text{th}}(t, \xi_1, \xi_2, \xi_3)}{dt} \right)^2 \right] + 2\xi_1\xi_2\kappa \right\| \quad (4)$$

with $\tilde{\xi} = (\xi_1, \xi_2, \xi_3) = (s_b^0, L_b, C)$ the vector of parameters to identify and R_f^{th} the theoretical flame radius.

The optimization algorithm used to minimize both objective functions (3) and (4) is the simplex algorithm, which is a direct research method [19]. Unlike other more traditional optimization methods in which function gradient information are necessary, the method used here does not require any information on the differentiability of the objective function. Indeed, at every step of the research, a new point in or near the current simplex is generated. The function value at this new point is compared to the function values at the vertices of the simplex, and generally one of the vertices is replaced by the new point, which gives a new simplex. This step is repeated until the simplex diameter is less than the desired tolerance.

Laminar burning speed

There are few works in the literature dealing with VOCs combustion [20] and none about the detailed kinetic mechanism of limonene. The expansion factor is therefore evaluated using the adiabatic flame calculation via the combustion reaction of limonene with air. Figure 4 illustrates the laminar burning speed of limonene/air mixtures as functions of equivalence ratio for different temperatures. We can see that these speeds versus equivalence ratio evolve as a bell-shaped curve with a maximal values at $\Phi = 1.1$. This laminar burning speed increases with initial temperature. The same tendency was observed in [21] for propane/hydrogen mixtures at 300 and 500 K.

The laminar burning speeds measured with the spherical expanding flame method can be given as a function of equivalence ratio and initial temperature. The temperature dependent part is based on the correlation of Metghalchi and Keck [22] with an additional term depending on the equivalence ratio. The final empirical expression of the laminar burning speed has the following form:

$$s_u^0 [\text{cm/s}] = s_u^{0\text{ref}} \left(1 + a_1 (1 - \Phi) + a_2 (1 - \Phi)^2 \right) \left(\frac{T_u}{T_u^{\text{ref}}} \right)^\alpha \quad (5)$$

where $s_u^{0\text{ref}}$ is the laminar burning speed at a reference point ($\Phi = 1$ and $T_u^{\text{ref}} = 353 \text{ K}$) given in cm/s, T_u (in K) is the unburned gas temperature and a_1 , a_2 and α are constants.

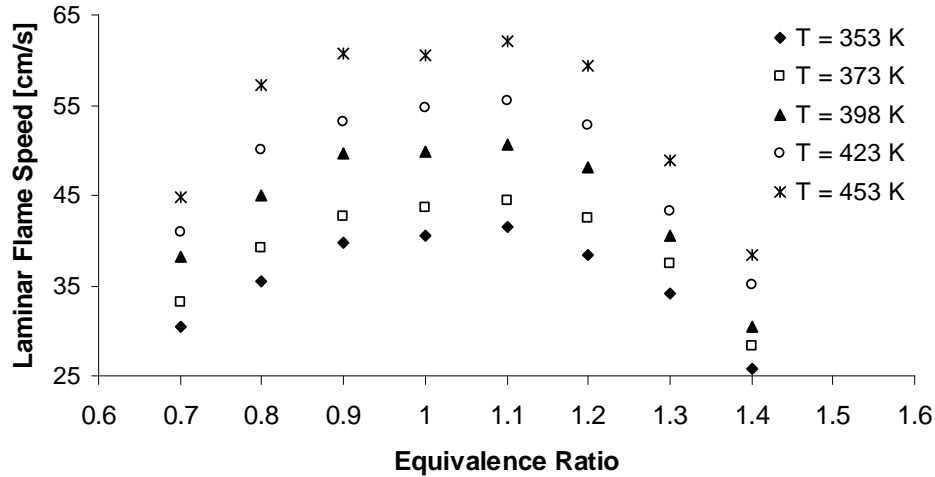


Figure 4. Laminar burning speeds of limonene/air mixtures as functions of equivalence ratio for different temperatures.

The best-fitting curve has been obtained by the least squares method. This method assumes that the best-fit curve is the curve that has the minimal sum of the deviations squared from a given set of data. The results of this fitting based on a minimisation genetic algorithm [23] are illustrated on Figure 5 and the values of the different coefficients are given in Table 2.

Coefficient	a_1	a_2	α
Value	-0.103	-2.563	1.757

Table 2. Fit parameters of the power law for the laminar burning speeds of limonene.

As we can see on Figure 5, the correlation of equation (5) is a good approximation of limonene experimental results for different initial temperatures.

There are no results in the literature on the laminar burning speed of limonene, the obtained values will therefore be compared to those of JP-10, which is an isomer of limonene (molecular formula $\text{C}_{10}\text{H}_{16}$) and to the ones of n-decane (same number of carbon atoms as limonene). The only available experimental data for JP-10 are given by Parsinejad et al. [24] at 450 K. Kumar and Sung [25] and You et al. [26] give respectively experimental and numerical laminar burning speeds of n-decane at 400 K. Therefore, simulations using the PREMIX code of the CHEMKIN package [27] at 398 K and 453 K are performed with the *San Diego* detailed kinetic mechanism of JP-10 [28,29].

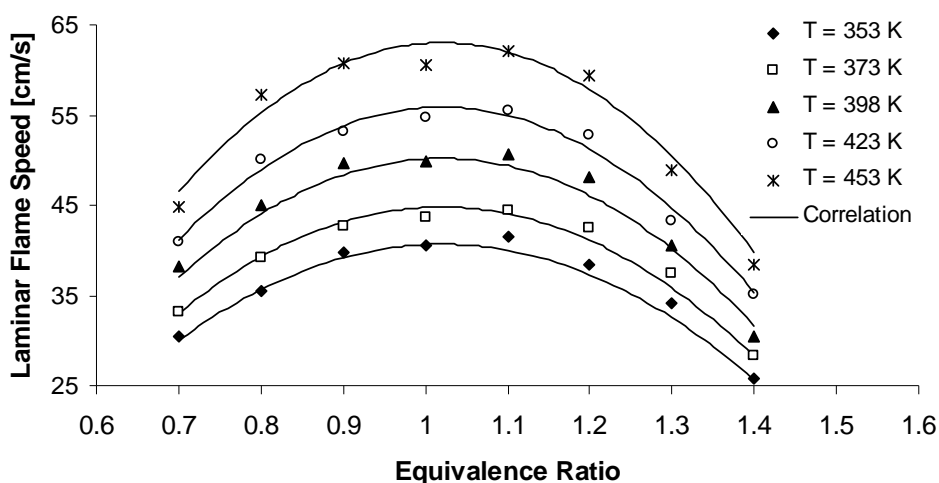


Figure 5. Best-fit curves of laminar burning speeds of limonene/air mixtures as functions of equivalence ratio for different temperatures.

Figure 6 illustrates the experimental results of limonene at 453 K and the experimental and numerical ones of JP-10 obtained respectively at 450 and 453 K.

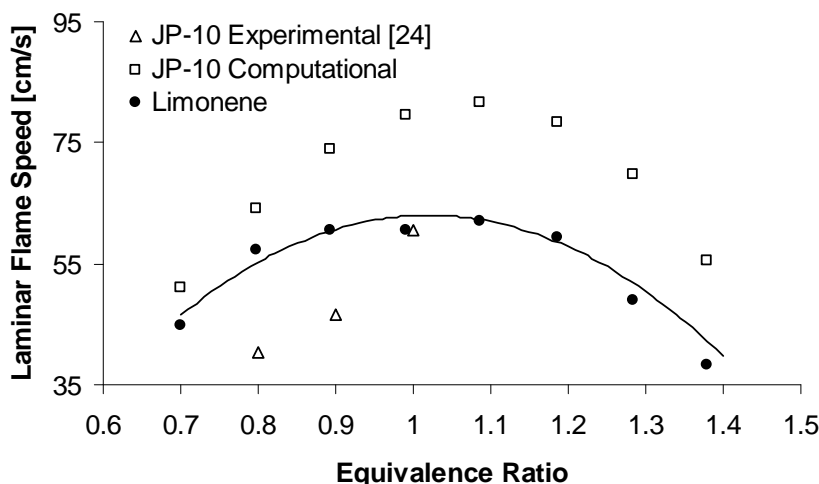


Figure 6. Laminar burning speeds of limonene/air mixtures at 453 K compared with those of JP-10. (■) Experimental values at 450 K; (□) Numerical values at 453 K; (—) limonene correlation.

We can observe on this Figure that numerical values of JP-10 are in good agreement with those of limonene for lean mixtures. From an equivalence ratio of 0.9 they overestimate the measured values. Experimental values given in [24] are lower than those of limonene for lean mixtures and close to them at the stoichiometry. The difference between JP-10 and limonene values can be explained by the difference in the experimental procedure (method based on the dynamic pressure rise in the spherical vessel for JP-10 values). Moreover, the gap between numerical values of JP-10 and those of limonene can be due to the fact that the *San Diego* mechanism is a semi-detailed kinetic mechanism and all the intermediate species are not taken into account in the calculation.

Figure 7 compares the measured values of limonene at 398 K with the experimental and numerical results of n-decane at 400 K as well as with those of JP-10 at 398 K. This Figure clearly exhibits that for all equivalence ratios, numerical results of JP-10 are very close to the

numerical ones of n-decane obtained via the detailed kinetic mechanism of You et al. [26]. This similarity between JP-10 and n-decane has also been observed by Seiser et al. [29] for diffusion flames. When it comes to experimental values of n-decane, they are in good agreement with those of JP-10 up to the stoichiometry and become higher than them for rich mixtures. The values of n-decane of the literature as well as those obtained with the PREMIX code for JP-10 are close to the measured ones of limonene for lean mixtures and become higher for other equivalence ratios.

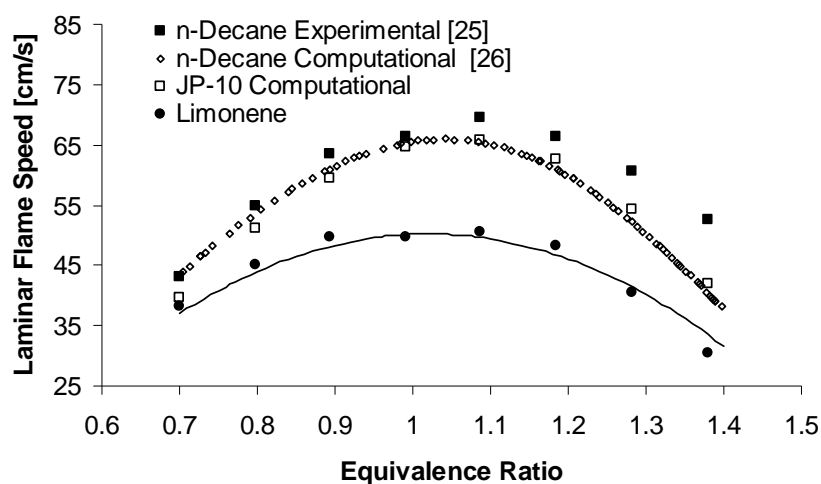


Figure 7. Laminar burning speeds of limonene/air mixtures at 398 K compared with those of n-decane and JP-10. (■) Experimental values of n-decane at 400 K; (◇) Numerical values of n-decane at 400 K; (□) Numerical values of JP-10 at 398 K; (—) limonene correlation.

Markstein length

Markstein length is a key parameter to characterize premixed flame stability. Its determination for limonene/air mixtures for different temperatures is based on the methodology described in Section 2. Figure 8 illustrates the influence of equivalence ratio and initial temperature on the Markstein lengths, quantifying the flame/stretch interaction for limonene/air premixed flames.

Very few data are reported in the literature for so heavy molecules (number of carbon atoms ≥ 10). Nevertheless, we can note the contribution on the Markstein length of n-decane/air mixture at 400 K for equivalence ratios ranging from 0.7 to 1.6 [30]. Experimental results show that Markstein length decreases when equivalence ratio increases with a decreasing steeper for equivalence ratios higher or equal to 1.1. The initial temperature effect on L_b can be neglected because L_b values are almost constant for different temperatures. This influence has already been noticed for methanol/air and ethanol/air mixtures [31,32]. We can also observe the sign change between the equivalence ratios 1.3 and 1.4, which corresponds to the stable to unstable flames transition. A similar tendency has been observed for n-decane with a transition between equivalence ratios 1.2 and 1.3 [30].

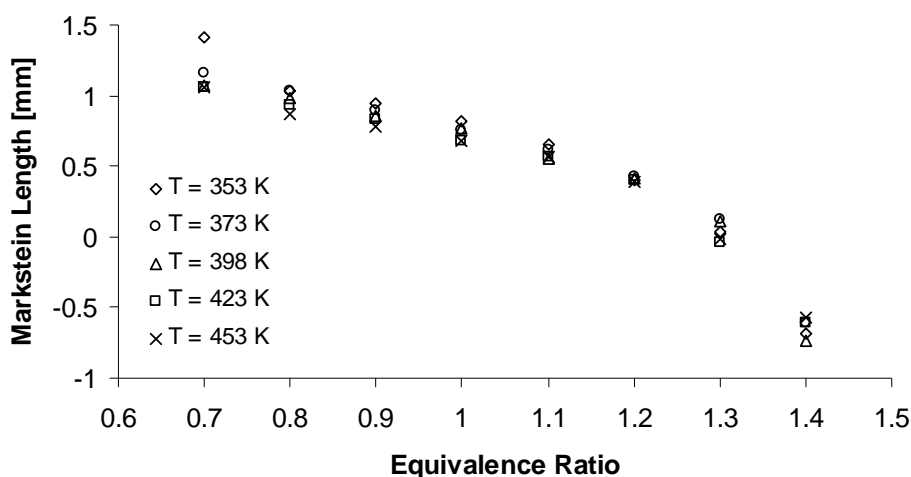


Figure 8. Markstein lengths of limonene/air mixtures as functions of equivalence ratio for different temperatures.

Conclusion

The present study deals with the experimental determination of the emissions and combustion characteristics of one of the main VOC emitted by a typical Mediterranean plant, namely *Rosmarinus Officinalis*. The emission experiments consist in placing a *Rosmarinus Officinalis* shrub into an emission chamber and to analyze the emitted VOCs. The experimental technique used in this work to determine these VOCs combustion characteristics is the spherical expanding flame method with a nonlinear extraction methodology. The experimental setup consists in a spherical vessel equipped with an optical system and a high speed camera for the visualisation of the flame front expansion.

The PREMIX code of the CHEMKIN package has been used to calculate the laminar burning speeds via the *San Diego* kinetic mechanism of JP-10, which is an isomer of limonene. The measured values have been compared to the numerical and experimental ones of JP-10 and n-decane found in literature. Experimental values of JP-10 at 450 K are close to the ones of limonene at the stoichiometry and lower than them for lean mixtures. Values of JP-10 simulations are in good agreement with those of limonene for lean mixtures (equivalence ratio lower than 0.9) at the same temperature. Experimental results of n-decane and numerical ones of JP-10 and n-decane at 400K are close to the measured values of limonene for lean mixtures.

Regarding Markstein lengths of limonene, we can say that they decrease when equivalence ratio increases for each initial temperature and they are independent from initial temperature. The transition between stable and unstable flames appears between equivalence ratios 1.3 and 1.4.

In the next stage of this work, we will compare the premixed flame speeds of limonene to the ones reported in real accelerating forest fires accidents in order to enhance the VOCs cloud ignition hypothesis to explain this phenomenon.

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