A volatile organic compounds flammability approach for accelerating forest fires

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Abstract

In this paper the accelerating forest fire phenomenon for three real accidents is investigated. This phenomenon is studied using the hypothesis of the ignition of a Volatile Organic Compounds (VOCs) cloud accumulated in canyons. By heating a *Rosmarinus officinalis* plant in a specific hermetic enclosure, fourteen VOCs are identified and quantified as temperature functions. The theoretical flammability limits of those components are calculated by means of empirical correlations. Froude scaling law is applied to present laboratory results to find the concentrations of VOCs at canyon scale. The comparison of the flammability limits with the obtained concentrations shows that the emitted VOCs can lead to an accelerating forest fire.

Keywords: Rosmarinus officinalis, VOCs emission, flammability domain, Froude scaling law, accelerating forest fire.

1 Introduction

Forest fires cause important damages in terms of ecological and economical issues and human lives every year. Some fires with normal behavior suddenly start to propagate at unusual and very fast speed. They are called eruptive fires by Viegas [1], fires flashover according to Dold et al. [2] or accelerating forest fires by Chetehouna et al. [3]. The term eruptive refers to the continuous rise of the fire rate of spread and flashover to its unexpected character.

There have been many accidents over the last half century where eruptive fires were reported [4–8]. In France, sixteen firefighters were killed during the

last fifteen years because of this phenomenon [9]. The more investigated case is the accident of Palasca (Corsica Island) in 2000, where survivors declared to have been surrounded by a "lake of fire" [2]. In Portugal, more than fifty persons lost their lives since 2003 [10, 11]. More recently, the Kornati accident in Croatia in 2007 killed twelve persons [7]. In Greece, also in 2007, more than seventy five persons lost their lives [12].

Up to now, the mechanisms to explain this kind of forest fire are not totally well known, as there are several phenomenological approaches for this phenomenon in the forest fires literature. One of the most recent mechanisms, proposed by Viegas [1, 13], suggests that the "fire eruption" is the consequence of the feedback effect of the convection induced by the fire. Another approach is that the acceleration of the rate of spread is caused by flow attachment in the direction of the fire propagation, according to Dold and Zinoviev [14].

In this paper, we explore the possibility of explaining the sudden acceleration of the fire as a consequence of the inflammation of the Volatile Organic Compounds (VOCs) emitted by fire heated vegetation and accumulated in the terrain ahead of the fire front for specific geometrical configurations such as canyons. Indeed, Chetehouna et al. [3] have shown using a simple extrapolation from laboratory experiments that the concentration of the VOCs at field scale is in the flammability domain (i.e. between the Lower Flammability Limit and the Upper Flammability Limit) of the α-pinene, which is the main constituent emitted by *Rosmarinus officinalis* plants.

The aim of this paper is to investigate more deeply this hypothesis by comparing the concentration of the VOCs mixture at canyon scale obtained by Froude scaling law for three accidents with the computed flammability limits. This approach assumes that the canyon is located in a place with a wind lull so that the VOCs accumulation is not modified by the atmospheric wind nor by the one induced by the flames. The sudden inflammation of these VOCs can possibly happen due to a firebrand coming from the fire front.

The second section is devoted to the description of the experimental protocol and to the presentation of the VOCs emissions at laboratory scale. In the third one, we will use an empirical method to determine the flammability limits of pure compounds at a reference temperature. The dependence in temperature is obtained by applying two correlations to those flammability limits. The flammability domain of the VOCs mixture is given by Le Chatelier's law. The last section is dedicated to the derivation of a relationship giving the VOCs concentration at canyon scale by means of Froude scaling law. Using a geometrical characteristic of the canyon shape, we will compare the VOCs concentrations of three real accidents (South Canyon, Palasca and Kornati) with the flammability domain provided in the previous section.

2   Volatile organic compounds emission in a hermetic enclosure

In this work, about thirty *Rosmarinus officinalis* plants were used to determine the effects of plant temperature on the emission of VOCs. These plants were

placed in a hermetic enclosure and were heated by a radiant panel. The hermetic enclosure with the dimensions of $100 \, \text{cm} \times 100 \, \text{cm} \times 134 \, \text{cm}$ was designed in cellular-concrete material with a thickness of 7 cm and its volume was 1.2 m³. The radiant panel is constituted of 16 black ceramics plates of a 144 cm² surface providing a maximal radiative heat flux around $84 \, \text{kW} \cdot \text{m}^{-2}$ (Figure 1).
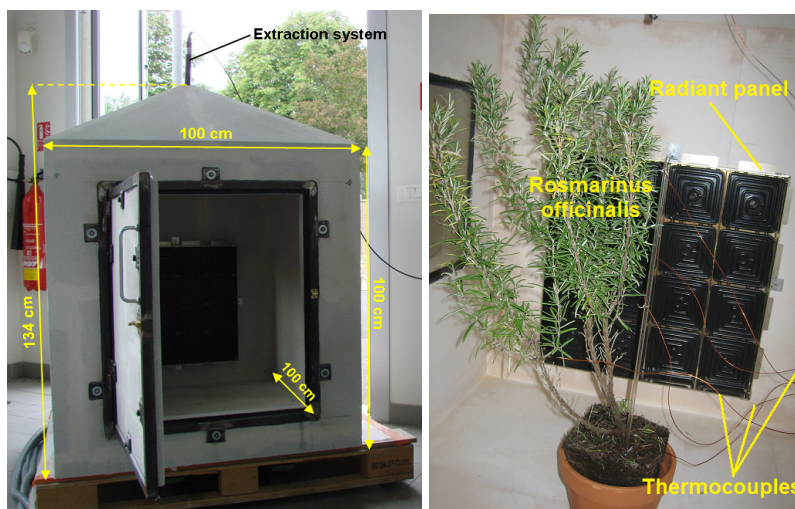

Figure 1:   Pictures of the experimental setup.

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 [3].

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 30 and 210 °C to simulate the heating of plants by a fire front before the pyrolysis phase (about 250 °C). The VOCs mixture (14 compounds identified) was characterized by high contents of monoterpenes hydrocarbons. Indeed, the main components were α-pinene, limonene, camphene, myrcene and β-pinene. The same compounds were observed by Ormeño et al. [15] for the study of the VOCs emissions by *Rosmarinus officinalis* under natural conditions. Figure 2 illustrates the evolution of the major constituents and the total VOCs emissions as a function of the plant temperature.
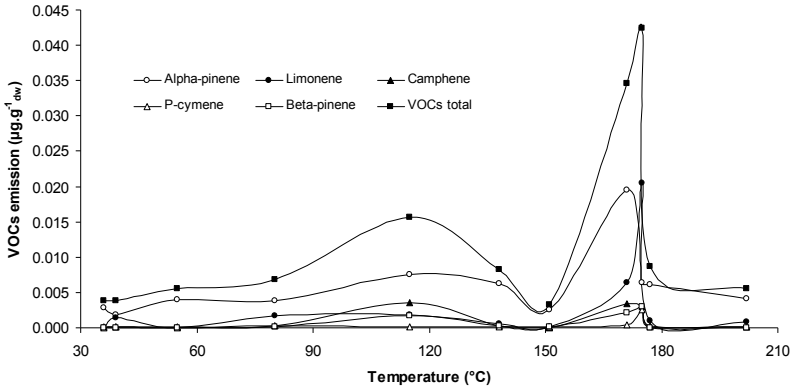
Figure 2: Main and total VOCs emission as function of temperature.

It was noticed from this figure that the VOCs emission increases with the plant temperature until 175°C. The same tendency was observed by Barboni [16] for others Mediterranean tree species such as needles of *Pinus nigra* and *Pinus pinaster*. The VOCs mixture amount at 175°C is 8 times higher than the one measured at 50°C. Moreover, we can see an increase of VOCs production around 120°C due to the transport of the VOCs by the evaporation process. Knowing that the boiling temperature of monoterpenes is about 154°C, these molecules would be in a liquid or in an equilibrium liquid-vapour state below this temperature. As a consequence, for the temperatures higher than this value, the VOCs emission increases rapidly to a maximum at 175°C. In this temperature range, the total emission of the VOCs is about 4 times more important than in the range 50–120°C. After 175°C, we can observe a significant decrease of the VOCs amount that can be explained by the thermal degradation of the terpenic molecules [16].

3 Flammability limits of a volatile organic compounds mixture

As mentioned in the previous section, 14 VOCs emitted by *Rosmarinus officinalis* and their proportion in the mixture have been identified at different temperatures before the pyrolysis phase. In this section, we will calculate the flammability domain of this VOCs mixture.

The lower and upper flammability limits of a VOCs mixture can be expressed by:

$$LFL_{mix}\left[\mathrm{g}\cdot\mathrm{m}^{-3}\right] = 10\frac{LFL_{mix}\left[\%\right]}{V_m}W_{mix} \tag{1}$$

$$UFL_{mix}\left[\text{g}\cdot\text{m}^{-3}\right] = 10\frac{UFL_{mix}\left[\%\right]}{V_m}W_{mix} \tag{2}$$

where $LFL_{mix}\left[\%\right]$ and $UFL_{mix}\left[\%\right]$ are respectively the lower and upper flammability limits in volume percentage, $W_{mix}\left[\text{g}\cdot\text{mol}^{-1}\right] = \dfrac{1}{\displaystyle\sum_i \dfrac{y_i}{W_i}}$ is the molar weight of the mixture with y_i being the mass fraction of the ith VOC and $W_i\left[\text{g}\cdot\text{mol}^{-1}\right]$ its molar weight. $V_m\left[\text{L}\cdot\text{mol}^{-1}\right]$ is the molar volume that depends on the temperature as:

$$V_m\left[\text{L}\cdot\text{mol}^{-1}\right] = 8.205\times10^{-2}(T+273) \tag{3}$$

where $T\left[°\text{C}\right]$ is the temperature of the VOCs mixture.

The flammability limits $LFL_{mix}\left[\%\right]$ and $UFL_{mix}\left[\%\right]$ can be found with the Le Chatelier's formula [17, 18]:

$$LFL_{mix}\left[\%\right] = \frac{1}{\displaystyle\sum_i \frac{x_i}{LFL_i\left[\%\right]}}, \quad UFL_{mix}\left[\%\right] = \frac{1}{\displaystyle\sum_i \frac{x_i}{UFL_i\left[\%\right]}} \tag{4}$$

where $LFL_i\left[\%\right]$ and $UFL_i\left[\%\right]$ are respectively the lower and upper flammability limits in volume percentage of the ith compound of the VOCs mixture and x_i its mole fraction given by

$$x_i = \frac{\dfrac{y_i}{W_i}}{\displaystyle\sum_i \dfrac{y_i}{W_i}} \tag{5}$$

Several methods are available in the literature to estimate the lower and upper flammability limits of pure compounds. These methods can be divided into four categories: empirical equations [19–21], critical flame temperature correlations [22, 23], structural group contribution methods [24] and neural network methods [25]. As empirical equations are easy to use (i.e. we need only the molecular formula of the compound) and give relevant results according to the previous authors, we will use them in this paper.

The lower and upper flammability limits in volume percentage $LFL_i\left[\%\right]$ and $UFL_i\left[\%\right]$ of the ith VOC, at the reference temperature 25°C, are given by the Gharagheizi [20, 21] relations:

$$LFL_{i(25°C)}[\%] = 0.76022 - 3.57754\, PW5 - 1.47971\, AAC$$
$$+8.57528\, SIC0 - 0.01981\, MLOGP \tag{6}$$

$$UFL_{i(25°C)}[\%] = 10.35415 - 1.35486\, Jhetv - 42.28779\, PW5$$
$$+18.59571\, SIC0 + 0.98203\, MATS4m \tag{7}$$
$$-0.68363\, MLOGP$$

The different parameters in these relations are molecular descriptors associated to each VOC and their values are available online on the Milano Chemometrics and QSAR Research Group website. These molecular descriptors are defined in Table 1.

Table 1:   Definition of the molecular descriptors.

Molecular descriptor	Type	Definition
$PW5$	Topological descriptors	Path/walk 5 Randic shape index
AAC	Information indices	Mean information index on atomic composition
$SIC0$	Information indices	Structural information content (neighborhood symmetry of 0-order)
$MLOGP$	Molecular properties	Moriguchi octanol-water partition coefficient (log P)
$Jhetv$	Topological descriptors	Balaban-type index from van der Waals weighted distance matrix
$MATS4m$	2D Autocorrelations	Moran autocorrelation-lag 4 weighted by atomic masses

We can obtain the flammability limits as function of temperature by using equations (6) and (7) coupled with the relations of Arnaldos et al. [26] and Zabetakis [27] respectively:

$$LFL_i[\%] = LFL_{i(25°C)}[\%]\left(1 - 7.8 \times 10^{-4}(T - 25)\right) \tag{8}$$

$$UFL_i[\%] = UFL_{i(25°C)}[\%]\left(1 + 7.21 \times 10^{-4}(T - 25)\right) \tag{9}$$

4   Scaling law and accelerating forest fire cases

Over the last decade, many fire studies implying laws that govern the change in scale - scaling laws - have been discussed by several authors. Hwang and Edwards [28] have shown with numerical simulations that the Froude-scaling law is a good approximation for tunnel fires between model and full-scale. Roh et al. [29] have done experiments on heptane pool fire in tunnels using Froude

scaling and have found proportionality between ventilation velocity and heat release rate.

In forest fires literature, we can notice the recent contribution of Pérez et al. [30]. These authors have used a dimensional analysis to find the scaling laws and have studied the effect of changing scale in forest fires experimentation.

To quantify the VOCs concentration at field scale in the canyon geometry proposed by Viegas [1], we will apply the Froude scaling law to our laboratory experiments. The Froude scaling law [31] consists in the preservation between model scale and full scale of the Froude number defined as the ratio of inertia forces to gravitational forces. So, we can write:

$$Fr = \frac{u_{lab}^2}{gL_{lab}} = \frac{u_{can}^2}{gL_{can}} \tag{10}$$

where $g \left[\text{m} \cdot \text{s}^{-2} \right]$ is the gravitational acceleration, $u \left[\text{m} \cdot \text{s}^{-1} \right]$ and $L \left[\text{m} \right]$ are respectively characteristic values of velocity and length. Subscript "*lab*" refers to laboratory scale and subscript "*can*" to canyon scale. A straightforward calculation from equation (10) gives:

$$\frac{u_{can}}{u_{lab}} = \sqrt{\frac{L_{can}}{L_{lab}}} \tag{11}$$

The concentration of VOCs in the hermetic enclosure and in the canyon at the sampling location and at different temperatures is given by the following relation [3]:

$$C_k \left[\text{g} \cdot \text{m}^{-3} \right] = \frac{\dot{m}_k \cdot \Delta t_k}{Q_v \cdot \tau} \tag{12}$$

where $\dot{m}_k \left[\text{kg} \cdot \text{s}^{-1} \right]$ and $\Delta t_k \left[\text{s} \right]$ are respectively the mass flow rate of the VOCs emission and the heating time at scale k (*can* or *lab*). $Q_v = 150 \text{ mL} \cdot \text{min}^{-1}$ is the flow-rate of gases extracted by the pump and $\tau = 10 \text{ min}$ is the sampling time; they are scaling invariants.

Then, we have:

$$C_{can} = C_{lab} \frac{\dot{m}_{can}}{\dot{m}_{lab}} \frac{\Delta t_{can}}{\Delta t_{lab}} \tag{13}$$

The mass flow rate of the VOCs emission can be defined as

$$\dot{m}_k = \rho u_k L_k^2 \tag{14}$$

with $\rho\left[\text{kg}\cdot\text{m}^{-3}\right]$ the density of the VOCs mixture, $u_k\left[\text{m}\cdot\text{s}^{-1}\right]$ their emission velocity and $L_k\left[\text{m}\right]$ a characteristic length deduced from the surface occupied by vegetation at scale k.

Based on the relation (14), the ratio of the mass flow rates and heating times are:

$$\frac{\dot{m}_{can}}{\dot{m}_{lab}} = \left(\frac{L_{can}}{L_{lab}}\right)^{\frac{5}{2}} \tag{15}$$

$$\frac{\Delta t_{can}}{\Delta t_{lab}} = \sqrt{\frac{L_{can}}{L_{lab}}} \tag{16}$$

Using the relations (13), (15) and (16), the VOCs concentration in the canyon can be given by the following expression:

$$C_{can} = C_{lab}\left(\frac{L_{can}}{L_{lab}}\right)^{3} \tag{17}$$

Now, we will apply this formula to three real accidents which occurred in USA (South Canyon accident, 1994), France (Palasca accident, 2000) and in Croatia (Kornati accident, 2007) described respectively by Butler et al. [5], Dold et al. [2], Viegas et al. [7] and Viegas [8]. The canyon characteristic lengths of these accidents are determined using the burned area where the phenomenon happened and the canyon geometry given by Viegas [1] and illustrated in Figure 3. These canyon characteristic lengths L_{can} can be calculated by the following relation:

$$L_{can} = l\cdot\cos\left(\frac{\theta}{2}\right) \tag{18}$$

where θ is the canyon angle and $l = \sqrt{\dfrac{A_{can}}{2}}$ with $A_{can} = 120$ ha, 6 ha and 10 ha for the South Canyon, Palasca and Kornati accidents respectively.

By means of the hermetic enclosure results and the equations (17) and (18), we can plot in Figure 4 the evolution of the VOCs mixture concentration involved in these three accidents and the VOCs mixture flammability limits versus temperature.

As we can see in this Figure, the VOCs concentrations under a particular climatic condition (without wind) for the large scale calculations (South Canyon, Palasca and Kornati accidents) are in the flammability domain for 6, 9 and 6 values of temperature respectively. These results show that under certain
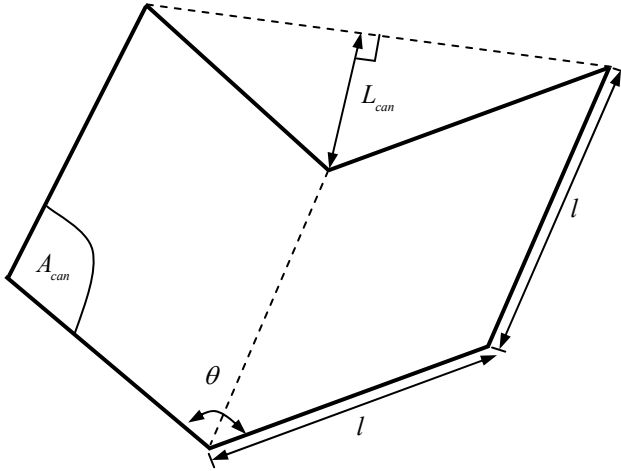
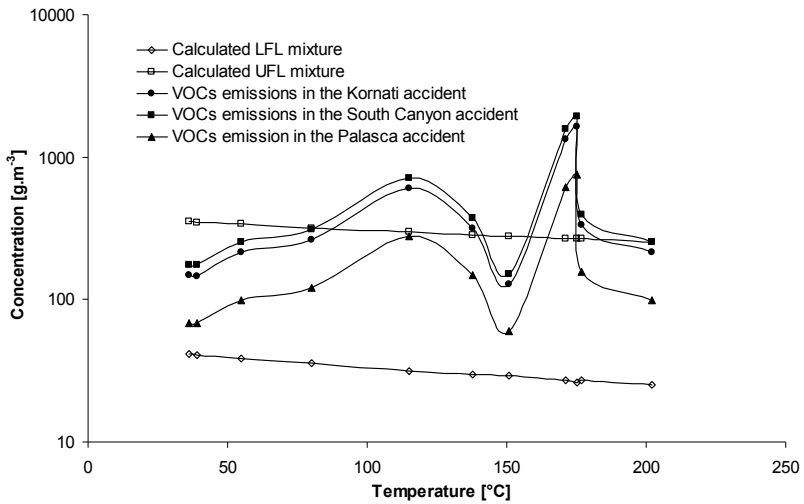Figure 3:   Schematic configuration of canyon shape.

Figure 4:   Comparison between VOCs mixture flammability limits and its concentrations in three real accidents.

conditions of vegetation type, climate and topography, it could be possible to have a flammable gas mixture in the vicinity of the vegetation ahead of the fire that could lead to a gaseous flame propagation and to the development of an accelerating fire triggered by this gaseous combustion process for those accidents.

Let us notice that this approach based on two geometrical parameters (the burned area A_{can} and the canyon topology depending on the angle θ) and on the emitted VOCs flammability limits is an explanation for the "lake of fire" observed in the Palasca accident [2] and for the acceleration of the rate of spread in the South Canyon accident. Concerning the Kornati accident, this approach can be considered as an alternative way to the eruptive fire theory developed by Viegas [1] and applied to this accident [7].

5 Conclusion

The present study is conducted on the relation between the VOCs emissions and their potential to cause an accelerating forest fires. It was found with laboratory experiments that *Rosmarinus officinalis* plants heated by external radiant heat flux emit fourteen VOCs, mainly monoterpenes hydrocarbons. The concentration of this gas mixture at canyon scale was calculated from these experimental results by means of Froude scaling law, assuming that there is no flow of VOCs out of the canyon space. The estimation of VOCs concentrations in canyons where three real accidents occurred (South Canyon, Palasca and Kornati), based on these hypothesis, has shown that their values can be in the calculated flammability domain of the gas cloud. Consequently, this phenomenological approach can be used to explain some real cases when those conditions are met. In such conditions, this process can be considered as an alternative explanation to the feedback effect of the convection induced by the fire [1] and to the flow attachment in the direction of the fire spread [14]. It will be interesting to realize in future work experimental studies of VOCs emissions at real scale (in canyons) and to compare them with the obtained results.

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