Combustion Characteristics of Two Biogenic Volatile Organic Compounds: I-fenchone and 3-hexen-1-ol

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1 Introduction

The Volatile Organic Compounds (VOCs) are mostly composed of carbon and hydrogen and have the particularity to readily vaporize. For the European Union, a VOC is « any organic compound having an initial boiling point less than or equal to 523 K measured at a standard atmospheric pressure of 101.3 kPa and can do damage to visual or audible senses » [1]. The VOC family gathers many thousands of compounds that fall into the following families:

- Aliphatic acyclic hydrocarbons,
- Alicyclic hydrocarbons derivated from aliphatic serie (e.g. terpenes),
- Aromatic or polyaromatic hydrocarbons (PAH) containing one or several benzene cycles,
- Oxygenated hydrocarbons (e.g. terpenoids).

According to their composition (family and carbon atom number), VOCs are more or less volatile, soluble, oxidizable and therefore more or less degradable. Emissions of low-volatility organic compounds may be subdivided into two classes: semivolatile organic compounds (SVOCs) and intermediate volatility organic compounds (IVOCs) [2]. We consider that an organic liquid is volatile when it has between 5 and 8 carbon atoms (C_5 to C_8) and low-volatile when it has between 9 and 16 carbon atoms (C_9 to C_{16}). Let us notice that most of the alcanes containing between 1 and 4 carbon atoms (C_1 to C_4) are gaseous compounds. We can add that methane is not often taken into account due to its natural presence in the air, we will then work on non-methane volatile organic compounds (NMVOCs).

VOCs are emitted by combustion or by evaporation. They are divided into two categories, those from anthropogenic origin (AVOCs), and those from biogenic origin (BVOCs). The main AVOCs are due to petroleum-refining sector, even if VOCs are included in the composition of most of daily used products: paints, inks, sticks, removers, cosmetics, dissolvers... BVOCs presented in this paper, are emitted by biomass and particularly by aromatic plants that give off a strong odour for this reason. BVOCs represent 90% of global

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NMVOCs on Earth [3]. However, trends are reversed if we bring it to a town scale or a country scale. For instance, around 20% of the NMVOC emissions in France have a biogenic origin [4].

The main BVOCs are isoprene (base of most biologic compounds structure) and monoterpenes (components of resines and essential oils from the alicyclic hydrocarbon family). In fact, we can divide terpenes into different groups according to their C₅-chain-number: monoterpenes (C₁₀), mainly α -pinène, β -pinene, delta-3-carene, limonene and pinene, sesquiterpenes (C₁₅) and diterpenes (C₂₀). The other main BVOCs which are detected are terpenoids from the oxygenated hydrocarbons family. Terpenes and terpenoids are formed from the plant metabolism thanks to the base molecule aforementioned : isoprene (C₅H₈).

BVOCs present two main risks, a health risk and a flammability risk. In this paper, we will focus on the flammability risk at stake in several serious forest fires, responsible of killing numerous persons of whom mostly were firefighters [5-7]. These fatalities are caused by a phenomenon called accelerating forest fire. This kind of fire behaviour remains unexplained but a thermochemical hypothesis has been proposed to explain it [8-10].

This thermochemical hypothesis rests on the fact that lower flammable limit (LFL) of BVOC/air mixtures is low and can therefore probably be reached in a natural environment. Indeed, for BVOCs we can find LFL of less than 1%-volumic-concentration in air [11]. Moreover, recent works have shown that BVOCs emissions are more important at high temperature [12]. It is then possible, in the case of forest fires, that VOCs emitted by plants accumulate themselves with pyrolysis products and form a flammable mixture depending on the flame front propagation and the terrain topography – canyon topography seems particularly favourable to this phenomenon. In order to prevent any accident, it is therefore important to control that the limit concentration of BVOCs have not been exceeded. This control seems possible in the industrial sector but is much more difficult in a natural environment. This difficulty is increased by the fact that a very few literature exists about the combustion of BVOCs. This paper intends to present more results in this research field.

As aromatic plants and accelerating forest fires are very present in Mediterranean regions, BVOC emissions are principally considered from this type of vegetation. The aim of this paper is to provide additional results concerning the combustion behaviour of different BVOCs focusing on two compounds predominantly emitted by the Mediterranean vegetation: 1-fenchone ($C_{10}H_{16}O$) and 3-hexen-1-ol ($C_6H_{12}O$). These are the main BVOCs respectively emitted by *Lavandula stæchas* and *Cistus albidus* – two plant species widespread all over the Mediterranean region. In this work will be presented two important characteristics: their laminar burning speeds and their Markstein lengths so that we are able to know more about their flame stability and propagation. These results may be useful to the domain of fire risks and prevention as well as to combustion modelling.

2 Experimental section

Two types of experiments were performed, the first one to study the emissions of VOCs by heated plants and the second one to study the combustion characteristics of the emitted VOC emissions. We have taken samples of the leaves of these two typical Mediterranean shrubs, *Lavandula stæchas* and Cistus *albidus*. In order to measure the VOC emission of these plant leaves, we make use of a flash pyrolysis apparatus (CDS Pyroprobe 5150) which has already proved itself to characterize the thermal degradation of various materials [13-15]. About 2.5 mg of *Lavandula stoechas* leaves and about 7 mg of *Cistus albidus* leaves are inserted inside a quartz tube and heated up to the chosen temperature. Then the resistively heated coil of the apparatus heat the samples of leaves with a heating rate of 5 K.ms⁻¹ from room temperature to the selected temperature. We maintain the samples at this temperature during 30 s. The emitted VOCs are transported to the GC/MS apparatus via a heated transfer line using helium as carrier gas. GC/MS analyses are performed with a Thermo DSQ II–Trace Ultra GC fit out with a DB5 capillary column (30 m long, 0.25 mm i.d., film thickness 0.25 μ m). The column temperature was programmed from 333 to 473 K at a rate of 5 K.min⁻¹ and held for 5 minutes at 473 K. Mass spectra were recorded in the electron impact mode with ionization energy of 70 eV. On the left part of Fig. 1, a schematic overview of the described experimental setup is illustrated.

The laminar flame velocity measurements are made using a stainless steel spherical combustion chamber. On the right part of Fig. 1, we present a schematic overview of the experimental protocol. Before filling the chamber, vacuum is first created. The amount of gases introduced into the chamber is controlled with a thermal mass flow meter. Synthetic air (79.5% N2 and 20.5% O2) is used for the experiments. High purity 1-fenchone and 3-hexen1-ol (\geq 98%) are consecutively injected through a Coriolis mass flow meter. The 1-fenchone/air and 3-

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hexen-1-ol/air mixtures are heated up to a preheat temperature of 453 K and the range of equivalence ratio is chosen between 0.7 and 1.4 with a 0.1 step. An electric fan, located inside the chamber, mixes all the gases. Two tungsten electrodes are used to produce spark ignition at the center of the chamber. For each condition, measurements are repeated three times. The flame images are obtained by shadowgraphy. The temporal evolution of the expanding spherical flame is then analyzed. During the initial stage of flame expansion, the total chamber pressure is constant, so flame radii larger than 25 mm are not taken into account, corresponding to a total volume of burnt gases less than 1.6% of the chamber volume.



Fig. 1. Illustrations of the emission and combustion experimental setups. Left: Schematic overview of the emission setup. Right: Scheme of the spherical combustion chamber.

3 Results and discussion

Fig. 2 presents the distribution of the different VOC families emitted by the two plant species. For each one, results have been taken for the temperature of the maximal emissions. Maximal emissions for *Lavandula stæchas* was found at 453 K identifying six families of VOCs. Terpenoids derivated from monoterpene hydrocarbons (C_{10}) are the most emitted as we can observe in purple on the left chart pie and the major VOC is l-fenchone ($C_{10}H_{16}O$) with 35% of the total emissions. The second major family identified is the one of alcohol (in light blue) with cineol ($C_{10}H_{18}O$) representing 20% of the emissions. The other major family is the alicyclic hydrocarbons family with monoterpenes $C_{10}H_{16}$ and $C_{10}H_{14}$ (in red and navy blue) but the third major VOC emitted at this temperature is a terpenoid: camphor ($C_{10}H_{16}O$). Similar compounds were identified in essential oils of *Lavandula stæchas* by Hassiotis and Dina [16] who gave l-fenchone as the main compound followed by camphor and cineol. L-fenchone was also identified by Vokou et al. [17] as the major compound of essential oils of *Lavandula stæchas*.

Maximal emissions for *Cistus albidus* were found at 443 K. As one can see in the right part of Fig. 2, we identified four different families of VOCs : $C_{15}H_{24}$ (sesquiterpenes), $C_{15}H_{24}O$ and $C_{15}H_{26}O$ (sesquiterpenoids) and $C_6H_{12}O$ (alcohol). The main emitted compound is 3-hexen-1-ol, it represents around 70% of the total emissions. Similar results were found by Peñuelas and Llusia [18] for the emissions of *Cistus albidus* at ambient temperature. The main sesquiterpene identified is curcumene and we have also obtained significant amounts of zingiberene and aromendrene. These compounds were also detected by Ormeño et al. [19] in their study on terpene emissions released by plants in response to abiotic factors at ambient temperature. We can also observe that *Lavandula stæchas* emits more chemical families than *Cistus albidus*.

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Fig. 2. Distribution of the chemical formulas of VOCs emitted by each plant species at the maximal temperature of emissions. Right: *Lavandula stæchas* at 453 K. Left: *Cistus albidus* à 443 K.

After studying the emissions of VOCs by two typical Mediterranean species and identifying the major emitted compounds, it becomes interesting to investigate the combustion characteristics of these two major components. Fig. 3 and 4 illustrate respectively the laminar burning speeds and the Markstein lengths of 1-fenchone/air mixtures and 3-hexen-1-ol/air mixtures as functions of equivalence ratio at 453 K.



Fig. 3. Laminar burning speeds of 1-fenchone and 3-hexen-1-ol/air mixtures at 453 K and 1 atm as functions of equivalence ratio compared with those of α-pinene and JP-10.

Fig.3 presents laminar burning speeds of the two studied compounds compared with results of similar compounds found in the literature: α -pinene (a VOC mainly emitted by plant species) and JP-10 (C₁₀H₁₆, an isomer of α -pinene). We observe that laminar burning speeds of 1-fenchone fit α -pinene results for equivalence ratios ranging from 0.7 to 1.2. For higher equivalence ratios, 1-fenchone values become higher than α -pinene ones, approaching JP-10 numerical (PREMIX) values. Concerning 3-hexen-1-ol behaviour, it is similar to JP-10 numerical values for lean mixtures (equivalence ratios 0.7 and 0.8) and rich mixtures (equivalence ratios 1.2 and 1.3). For equivalence ratios around the stoichiometry (between 0.9 and 1.1), 3-hexen-1-ol values are lower than JP-10 numerical values and slightly higher than α -pinene ones. We notice that laminar burning speeds of the studied compound are on the same order of magnitude as similar molecules found in the literature. For both of the studied species, the maximal laminar burning speed is reached for an equivalence ratio of 1.1. For lean mixtures, laminar burning speeds are contained between 40 and 50 cm/s.

As to Markstein lengths, very few works in the literature give them for heavy molecules (> C_{10}). Nevertheless, we can note the contribution of Courty et al. [12,20] for *p*-cymene and α -pinene/air mixtures. These results along with the ones of the present study are presented in Fig. 4. Markstein lengths of l-fenchone and 3-hexen-1-ol are in agreement with *p*-cymene and α -pinene values; values are decreasing with the increase of equivalence ratios. We can see that the transition between stable and unstable flames (i.e. the transitions between positive and negative Markstein lengths) appears between equivalence ratios 1.3 and 1.4 for l-fenchone, α -pinene and *p*-cymene fuels. Contrarily, Markstein lengths of 3-hexen-1-ol stay positive in the studied range of equivalence ratios, showing the stability of the flames, even for rich mixtures.



Fig. 4. Markstein lengths as functions of equivalence ratios for l-fenchone and 3-hexen-1-ol/air mixtures at 453 K compared with those of p-cymene and α -pinene.

4 Conclusion

In this study we obtained additional results on emissions of BVOCs by typical Mediterranean shrubs. With adapted experimental setup and methodology we extracted combustion characteristics of 1-fenchone and 3-hexen-1-ol which appear to be the main VOCs respectively emitted by *Lavandula stæchas* and *Cistus albidus*. Results were compared with experimental and numerical ones of similar compounds available in literature. Obtained results will permit a better understanding of forest fires, taking into account the VOCs combustion in forest fires propagation physical models. They could also be useful for a validation of the thermochemical hypothesis to explain accelerating forest fires.

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