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DOMINGOS XAVIER VIEGAS
LUÍS MÁRIO RIBEIRO

TGA/TDA and Analytical Pyrolysis (Py/GC-MS) of Two Mediterranean Forest Species with Distinctive Flammability Characteristics: *Cupressus sempervirens L.* and *Quercus suber L.*

Rawaa Jamaladdeen*[1]; Imene BenBelkacem[2]; Bruno Coudour[1]; Laurent Lemée[3]; Christelle Roudaut[3]; Aicha Bouhafsoun[2]; Abderrezak Djabeur[2]; Hui-Ying Wang[1]; Jean-Pierre Garo[1]

[1] *Institut P', ENSMA ISAE, Université de Poitiers, Chasseneuil-du-Poitou, France, {rawaa.jamaladdeen, bruno.coudour, hui-ying.wang, jean-pierre.garo}@ensma.fr*
[2] *Laboratoire de Production et valorisation végétale et microbienne, Université des Sciences et Technologie Mohamed Boudiaf (USTO-MB), Oran 31000, Algérie, {imenoo13@hotmail.com}, {abouhafsoun@gmail.com}, {sidjabeur@yahoo.fr}*
[3] *IC2MP - UMR CNRS 7285, Université de Poitiers, Poitiers Cedex, France {christelle.roudaut, laurent.lemee}@univ-poitiers.fr*

**Corresponding author*

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Abstract

The frequencies of wildfires in the Mediterranean climate regions (MCRs) have amplified due to the increased temperatures and drought periods resulting from climate change. Vast areas of forests are consumed by wildfires and certain species are threatened by extinction due to their high flammability and weak thermotolerance to climate change whereas, other species with high thermotolerance are exploited as silviculture measures in forest management strategies. Canopy and litter foliage are the first ignitable structures in a forest fire. In this context, the foliar flammability characteristics of two fire resilient Mediterranean forest species are tested and compared on a laboratory scale; Quercus suber L. (Q.s.L.) and Cupressus sempervirens L (C.s.L). Thermo gravimetric/thermo differential analysis (TGA/TDA) and low- to high- temperature analytical pyrolysis tests and gas chromatography-mass spectrometry (GC-MS) were conducted on live and dry foliar samples of Lebanese C.s.L and Algerian Q.s.L. Branch and cork samples of Q.s.L were also pyrolyzed (Py/GC-MS) for their volatile content. The hemicellulose/cellulose degradation temperatures of C.s.L. were in the order of 30 to 50°C more than those of Q.s.L. Lignin degradation started later in the Q.s.L. and took place at temperatures higher than those of C.s.L. (≥30°C), while the heat release rates (HRR) were greater for the latter than the former in both degradation phases. The pyrolysis tests showed higher volatile content of C.s.L compared to Q.s.L. The high thermotolerance characteristic of C.s.L may be referred to its high terpene content which was negligible in Q.s.L given the fact that it is a non-monoterpene emitter oak species with no terpene storage compartments. The use of C.s.L as a fire barrier could be justified given their thermotolerance characteristic. Q.s.L. fire resilience is justified for their bark characteristics however; their foliage fire resilience should be further experimented.

1. Introduction

Climate change with increased temperatures and prolonged drought periods promote a positive trend in the frequency of wildfires in the Mediterranean climate. The Mediterranean vegetation is adapted to natural wildfires but is vulnerable to the abiotic stresses brought by the prolonged dry and hot summer seasons which is suspected to affect their BVOCs (biogenic volatile organic compounds) reserves. Therefore, an accurate determination of the flammability characteristics of the Mediterranean vegetation is needed in order to implement effective forest management strategies. Flammability descriptors define the vegetation ignitability, combustibility, consumability, and sustainability. However, the methods for evaluating these descriptors have not yet been standardized but are strongly linked to their BVOC reserves at the event of the wildfire. Cork oak or Quercus suber L. (Q.s.L.) and Cupressus sempervirens L. (C.s.L.) are abundant Mediterranean forest species with distinctive morphological characteristics. C.s.L. species which possess foliar monoterpene storage compartments (resin ducts) (Hamidpour et a. 2011) are recognized for their high thermotolerance characteristics and are being considered in silviculture measures as green barriers against wildfires (Della Rocca et al. 2015).

A cypress plantation in Spain (Valencia), was slightly affected by a wildfire that burnt all trees arounds whereas only 12.7% of the cypress trees were burned, 37.1% were dehydrated and 61.6% were not affected (Della Rocca et al. 2015). Although, this same species is dangerous as a house hedge because when it is regularly cut to form a clean hedge, dead fuel accumulates inside the trees. This dead fuel constitutes a powerful source of radiation once a fire reaches it. On the other hand, Q.s.L. found abundantly in countries of the Mediterranean basin and in Portugal, are considered non-monoterpene emitters because they are incapable of endogenous monoterpene production (Loreto 2002) and their photosynthesis is inhibited at temperatures >30°C (Delfine et al. 2000). Therefore, they possess the lowest thermotolerance levels amongst other Mediterranean forest species and are largely consumed in wildfires. The flammability and thermotolerance characteristics of the two species were investigated by undergoing thermogravimetric/differential thermal analysis (TGA/DTA) and low- to high-temperature pyrolysis testing (Py/GCMS) on foliar live and dry samples of the Lebanese Cupressus sempervirens L. and Algerian Quercus suber L. The TGA/DTA and Py/GC-MS tests were conducted in the IC2MP laboratories of the University of Poitiers, France.

2. Materials and Methods

2.1. TGA/DTA:

The device used is SDT Q600 (DSC-TGA) equipped with a horizontal dual-balance mechanism which provides a high level of accuracy in the measurements of weight and temperature differentials. 20 mg of live and dry foliar samples of the two species: Cupressus sempervirens L. and Quercus suber L. were tested in an air medium with a flow rate of 50 $mL.min^{-1}$ at a temperature range from 20 to 900°C with a ramp of 10°C/min. The same method was used to analyze branches and cork of Q.s.L., and compare seasonal (winter and summer) dry foliar samples of C.s.L.

2.2. PY/GC-MS

The pyrolyzer is a Frontier Lab EGA 2020 pyrolyzer equipped with an AS-1020E auto-shot sampler coupled with a GCMS (Shimadzu QP 2010 Ultra). GC separations were done using a SLB-5MS (Supelco) capillary column (30 m long, 0.25 mm i.d, 0.25 μm phase thickness). Low- to high- temperature pyrolysis experiments were done on seasonal live and dry foliar samples of Cupressus sempervirens L. and live and dry foliar samples in addition to branches and cork samples of Quercus suber L. The designated pyrolysis temperatures were correlated to the TGA/DTA results which defined the different degradation temperatures of the cellulose, hemicellulose and lignin of the vegetation species. Also we were interested to simulate the effects of the thermal stresses of the fire-front approaching the vegetation in an open forest fire. The program of the pyrolysis tests is shown in Table1.

Table1. Pyrolysis program and designated temperatures of the experiments

	Cupressus sempervirens L. (Foliar samples)	**Quercus suber L. (Foliar, wooden, cork)**
Single Shot	50 - 80 - 120 - 180	800
Double Shot	350 - 550	350 - 550
Triple Shot	120 - 350 - 550	

2.3. Materials

Dry foliar samples of C.s.L. were collected and transported by airplane from a Lebanese forest in the summer season in August with an average ambient temperature high at 28/30°C, and in the winter season in January with an average temperature low at 5/10°C and annual rainfall of 700 to 1000 mm. Live foliar samples were obtained from irrigated cut branches of the same tree in both seasons and brought to France to be experimented in 3 days period. The Q.s.L dry foliar samples branches and cork were collected randomly from a mature Quercus forest in M'sila, Algeria by our collaborated research team of the University of Oran, Algeria. The live foliar of Q.s.L. were taken from a 1year old Quercus tree planted in Algeria and transported to France and were cut at the day of experimenting. All specimens were stored in the lab freezer at temperatures (-21±1°C) prior and during the experiments. The experiments showed similar fuel moisture content between the dry and live samples of the two species.

3. Results

The TGA/DTA (Figures 1&2) provided the temperature evolution of the specimen degradation phases that are likely to occur in an open fire for each of the two species. First trough indicating the endothermic thermal dehydration (distillation/drying) followed by the first peak signaling the exothermic ignition of the semi volatiles resulting from the degradation of cellulose/hemicellulose. The second peak at the higher temperature ranges is due to the combustion of the partially charred biomass and the aromatics released from the degraded lignin. The temperature ranges for each of the processes allowed us to correlate them to their flammability descriptors: ignitability and combustibility.

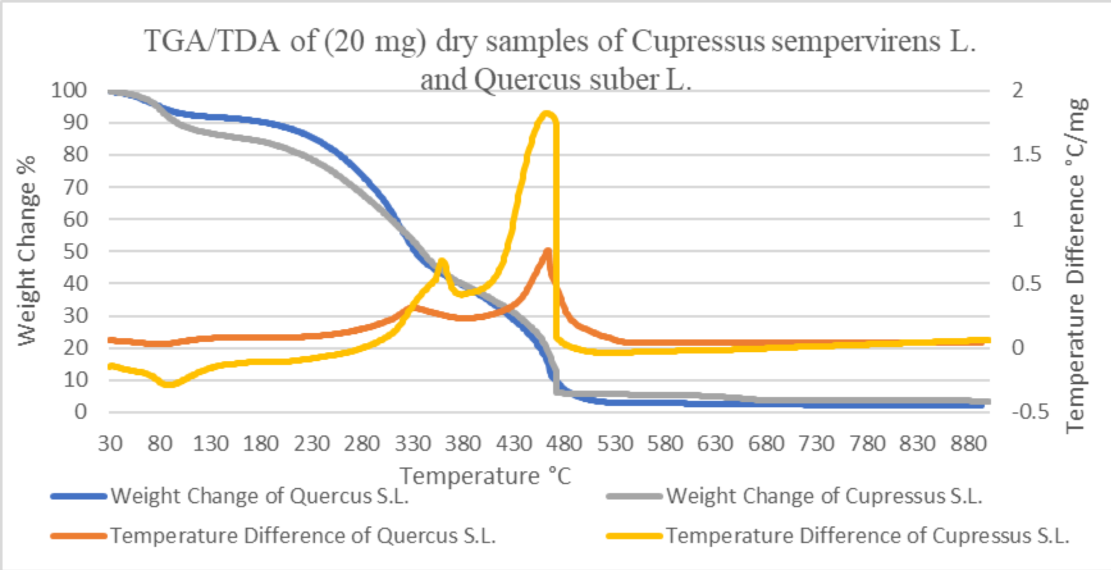

Figure 1- TGA/TDA of foliar dry samples of Cupressus sempervirens L. vs Quercus suber L.

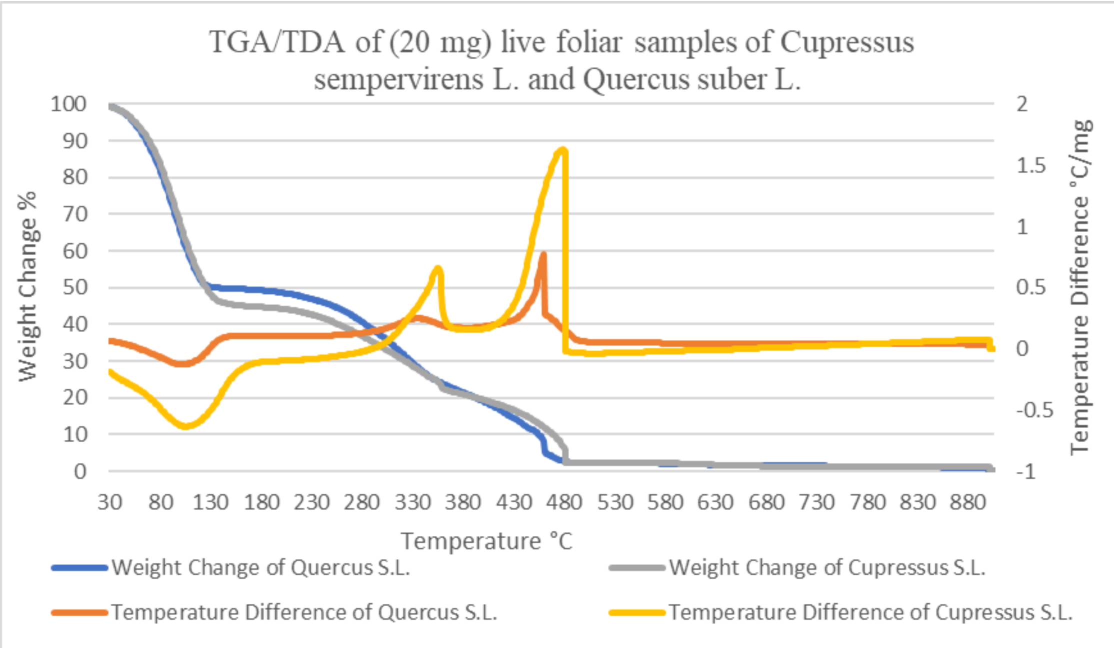

Figure 2- TGA/TDA of foliar live samples of Cupressus sempervirens L. vs Quercus suber L.

The time to ignition (TTI) (Dehane et al. 2017) or the ease to ignite (Fernandes et al. 2012) described vegetation ignitability. The combustibility is measured by HRR, and the consumability depends on the burnt mass residue. TGA/TDA of dry and live foliar C.s.L and Q.s.L. (Figure 1&2), showed cellulose degradation (first peaks) of C.s.L. at higher temperatures than those of Q.s.L and the inverse for lignin degradation (second peaks). The HRR in both degradation phases was higher C.s.L. compared to Q.s.L. Therefore, we can argue about the better combustibility of C.s.L. probably due to its larger volatile content. We were also able to compare the thermal degradation profiles of seasonal (summer and winter) dry foliar of C.s.L. (Figure 3). The thermotolerance of summer foliar C.s.L. is clearly greater than that of winter C.s.L., and the (HRRs) of the former were higher than the latter probably due to higher volatile reserves; a characteristic of resinous conifers.

Table 2. Temperature profiles of each degradation phase from the TGA/TDA of live and dry foliar samples of C.s.L. and Q.s.L.

	Vegetation Species	**Approximate Temperature range °C**		
		Thermal Dehydration	Hemicellulose/Cellulose Degradation	Lignin Degradation
Dry Foliar	Cupressus sempervirens L.	80 - 130	330 - 380	400 - 480
	Quercus suber L.	75 - 80	280 - 330	430 - 500
Live Foliar	Cupressus sempervirens L.	80 - 180	330 - 380	400 - 480
	Quercus suber L.	75 - 130	300 - 330	430 -50

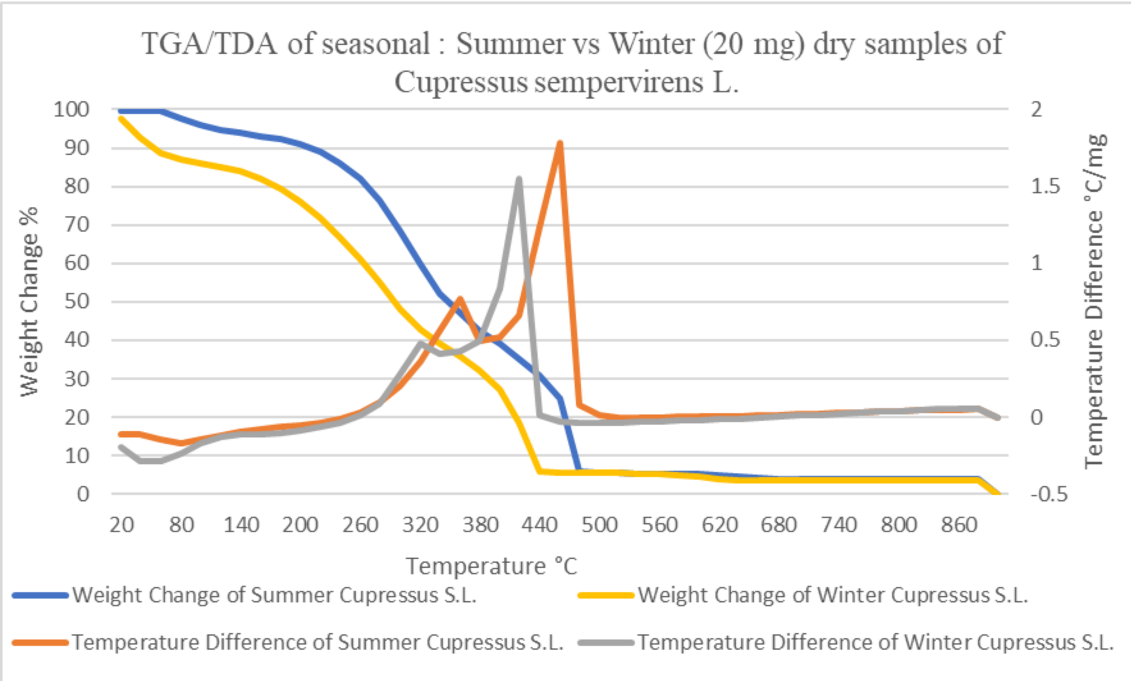

Figure 3- TGA/TDA of seasonal (summer & winter) foliar dry samples of Cupressus sempervirens L.

The Py-GC-MS experiments were conducted on the dry foliar samples of the two species. The pyrolysis products were identified on the basis of their GC retention times and by comparison of their mass spectra with those of standards and library data (NIST), (Figure 4). We identified terpene reserves (monoterpenes, sesquiterpenes, diterpenes) in the C.s.L. samples and none in the Q.s.L. (non -endogenous monoterpene emitter). Pyrolysis of Quercus cork released phenols of guaiacyl-type and syringyl type while the acetic acid indicated the thermal degradation of suberinic acids.

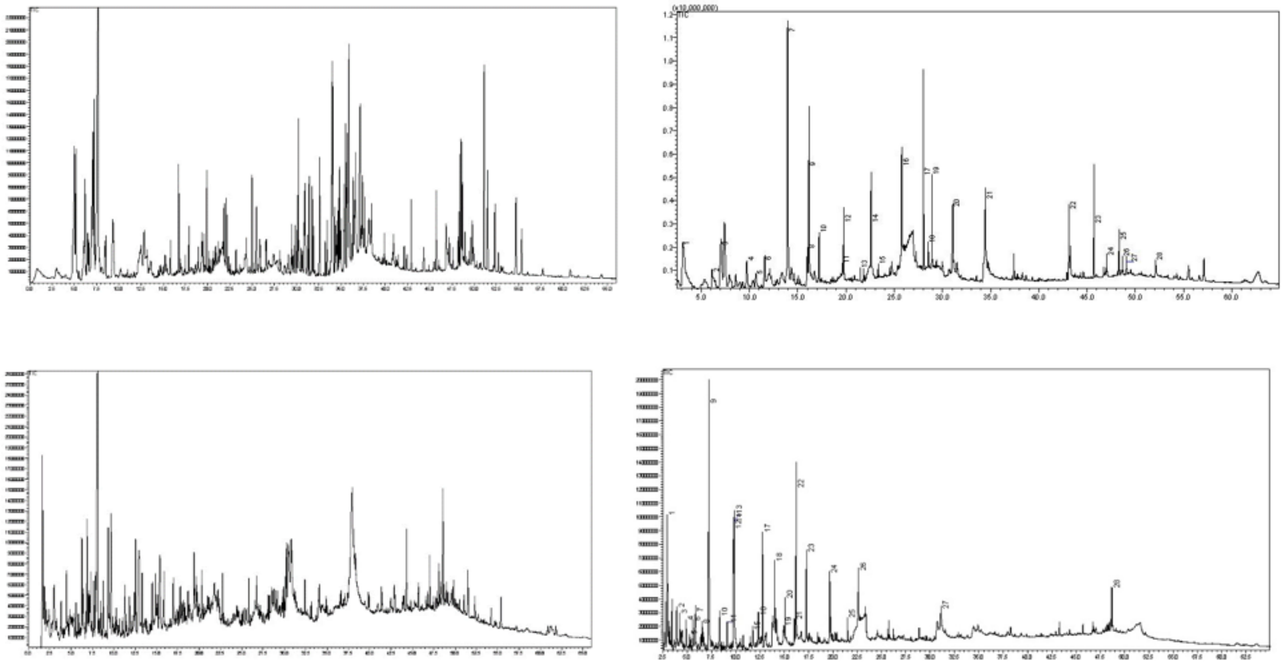

Figure 4- Pyrograms of dry C.s.L. (left) and dry Q.s.L. (right): up at 350°C, below at 550°C.

The aromatization of Q.s.L. to produce phenol and phenol homologues (i.e., methoxyphenol, dimethyl phenol, vinyl methoxyphenol, …) was remarkable at 350°C due to the degradation of lignin in dry foliar, branches and cork of with percentages of 51%, 71%, and 36%, respectively. These percentages increased remarkably at 550°C to 81%, 67% and 47%, respectively. The yield of suberin (insulation characteristic of Quercus suber) from cork pyrolysis was null at 350°C, 45% at 550°C, and 22,8% at 800°C. Phenol-derived compounds emerged humbly from C.s.L. dry foliar pyrolysis at 350°C while furanics (furfural, furan) of cellulosic origin and terpenes (mono, sesqui and di) were still dominant. Remarkably, sesquiterpenes were still identified from C.s.L. pyrolysis at 550°C and the percentages of mono aromatics (toluene), phenolics (phenol, methoxy-phenol, benzenediol) increased remarkably. Comparison between the pyrolysis products from dry foliar C.s.L. showed bigger reserves of VOCs in summer versus winter samples. Unlike the case of C.s.L., the degradation of Q.s.L. foliar lignin at 350°C (a temperature easily reached in wildfires), with the release of phenols and aromatics would accelerate flame propagation in wildfires hitting Quercus suber L. forests. The complete analysis of the experimental pyrolysis results will be presented in detail in the full paper edition.

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