Abstract: Most Mediterranean regions face a high risk to forest fires, estimation and anticipation of this risk modeled as a stochastic propagation process reproduces well some fire properties. This model needs information on the behavior of the bio-physical properties of vegetation associated to combustion. An experimental study to analyze the structure of a leaf of Laurel shrub at different biological stages is presented; it allows following the structural exchanges induced on the leaf by the effect of increasing temperature. For this purpose, both dielectric and TGA (Thermogravimetric Analysis)/DTA (Differential Thermal Analysis) was performed to a better understanding of the pyrolysis phenomenon. The results obtained provide information on the process of thermal degradation caused by fire. The evolution of the leaf impedance as a function of the applied frequency characterizes the moisture loss in plant species during pyrolysis. The dielectric response confirms the proposition to the equivalent circuit of the leaf as a composite of liquid and solid parts. The TGA/DTA results detected the behaviour of the solid parts in the fire under a constant heating rate, and were able to show all the transformation subjected by the Laurel leaf until ignition and all the gases released during it.

Key words: Impedance spectroscopy, TGA/DTA Analysis, pyrolysis, modeling, forest fire.

1. Introduction

Fire is a phenomenon known since hundreds of thousands of years but it still remains a difficult event to control and threatens millions of hectares of terrestrial forest and natural resources.

Several studies have been interested in modelling forest fires, this has led to the development of different propagation models, like for example SAFIR fire code and SWN (Small World Network) in order to minimize risk and improve the fire control and protection strategies [1, 2]. The model proposed in this study is a stochastic propagation model [1-3] that reproduces well some fire configurations [3], with a simulation time 10 to 100 times faster than real time. This model takes into account the intrinsic nature of the fire such as the local heterogeneity linked to the local wind and to the topography, the flame radiation, the weighting process due to the flame residence time and the activation (ignition) energy of the exposed combustible. But despite this, the physico-chemical operations of the spread of fire, as distinction of the residence time and combustion, the issued and received power and the ignition energy have not been fully elucidated.

In fact, the vegetable nature of forests is a multiphase complex; the ignition and the spread of fire involve physical and chemical mechanisms at different scales, where under a source of heat a pyrolysis process is started at the microscopic level of the plant cell. This leads to water evaporation and therefore to the emission of gases probably harmful and dangerous. Furthermore, the airflow brings oxygen which activates the combustion of these gases.

This thermal degradation process is strongly linked to the bio-chemical characteristics of cells hence is the
interest to study and characterize the structural and microscopic changes occurred during fire development.

Understanding the behaviour of plants under fire is the subject of several theoretical, numerical and experimental studies based on physic-chemical laws. One of the most recent experimental methods available is the dielectric spectroscopy which serves to acquire the variation in the dielectric properties of a material as a function of frequency of the signal, often under the action of an external field [4, 5]. This approach is commonly used to characterize the relaxation of polar liquid [6] and porous materials (soil, rock, plaster or concrete) [7, 8].

Besides the dielectric spectroscopy a TGA (Thermogravimetric Analysis) [9, 10] is recommended in order to have an accurate description of the pyrolysis process. This thermal analysis is commonly used to determine the rate of reaction of releasing or absorbing a substance under a flow of high temperature with a controlled environment [11].

The work done in this paper fits in the area of research on forest fires modelling. In this context, the efforts have been focused on the characterization of the structure and the composition of vegetation (wild Laurie) during the combustion in order to have information on the vegetation ability to spread fire by determining their ignition parameters and integrate it into the fire model proposed in Ref. [2].

During a fire privileged parts to start inflammation in a short time are the leaves and thin branches, which led us to analyze firstly a plant leaf. This unit is organized into three main tissues: a dermal tissue to cover the leaf components, a ground or fundamental tissue, where the maximum of leaf components are. It allows intercellular communication and circulations of the substances inside the cells. The last tissue is the vascular system which allows the ionic transfer and movement during the phenomenon of chlorophyll [12] (Fig. 1).

These fundamental units of the leaf have a different constitution of water, oils and solid material such as mitochondria, chloroplast and nucleus. But this does not prevent to model the leaf as a composite system of two main parts: liquid and solid (Fig. 2).

Fig. 1  Leaf tissue anatomy.
In fact, the chemical and biological exchange induced under the effect of light and the temperature in the leaf, act similarly to an electrical process. Where the ionic movements, which can take place in the aqueous medium of the plant cell under the effect of an external field being none other than electric charge motion (equivalent to electric current passing through a resistance according to Ohm’s law) which is used to model a resistor. Whereas at the cell membrane (solid part), the charges are spontaneously separated and deposited on either side of the membranes which thus form a virtual capacitor [12].

2. Materials

In order to study and characterize the thermal degradation of a leaf during a fire, one of the current non-destructive methods the impedance spectroscopy is used firstly. However, the TGA/DTA (Differential thermal Analysis) was used later for a better description of the pyrolysis phenomenon.

The first study was carried out on an impedance meter analyzer existing in the laboratory of non-crystalline materials at the University of Aveiro Portugal, the analysis were performed on circular samples (d 1E-2, h 2E-4) of laurel leaves at different moisture conditions and for several temperature cycles ranging from -50 °C to 150 °C with a frequency from 100 Hz to 1 MHz. These dielectric analysis require the vacuum and a thermal insulation to ensure the uniformity of temperature between the sample surface and its container.

The vacuum is carried out by an air evacuation system (air pump) to remove the maximum of moisture from the sample surface. However, the thermal insulation system allows the temperature increase without exchange with the external environment.

This system is composed of two coaxial glass cells dipped in a bath of liquid nitrogen (77.3 °K), both cells are separated from each other by a hollow space being filled initially by helium “He” to decrease the temperature.

Once reached the desired temperature, the helium will replaced by the vacuum to have a thermal insulation with the external environment. However, the internal cell containing the sample is completely filled with helium which ensures a good distribution of the heat.

This last cell (internal) is connected to 2 or 4 thermocouples to monitor the increment of the sample temperature. This increase of temperature is achieved by two armored parallel resistances to eliminate the magnetic effects.

Moreover, this increment is controlled by a PID (Proportional Integral Derivative) regulator that ensures the achievement of the desired critical temperature without exceeding it, where for every 5 °C; it stabilizes the temperature to allow the analyzer to take measurements of the dielectric parameters.

From another side, the TGA/DTA tests were performed on a Rheometric Scientific STA 1500 analyzer, which enables the STA (Simultaneous Analysis) of DTA and TGA existing in the Mechanical Engineering Department of the University of Coimbra Portugal.
This equipment contains a programmable furnace that can reach up to 1,500 °C with different heat rates from 0.2 °C to 60 °C/min by a step of 0.1 °C/min. It contains also a precision balance (400 mg) with a plate connected to the sample, a suitable closed system for controlling the atmosphere in the sample chamber and a cooling system of 1 bar of cold water.

The selection of the acquisition data and the test conditions is performed by software—Plus v6.5.5—connected to the furnace by a communication interface.

The TGA tests are often influenced by the size and homogeneity of the sample, nature of the gas and its flow rate, heating rate, the contact surface between the sample and the crucible bottom, and the position thereof in the palette of the sample holder.

The analysis was carried on laurel leaves at different moisture content values grinded in a powder sample of 13 mg for a range of temperature from 20 °C the ambient to 900 °C with a heating rate of 10 °C/min in a nitrogen environment.

4. Results and Discussion

The dielectric results shown in Fig. 3 indicate the existence of a relaxation frequency depending on the temperature value which is certainly due to the structural changes occurring in the leaves under a field of temperature.

At this characteristic frequency, the electrical conductivity is higher showing the existences of a considerable amount of aqueous media (water) which allows an easy flow of current due to the ionic movement. However, this amount decreased each time the sample is exposed to a temperature cycle (Fig. 3).

A weird behavior is shown between the 2nd and 3rd cycle where a slight increase in the electrical conductivity is observed that is probably due to the change of the sample size when it loses water. For the

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**Fig. 3**  Electrical conductivity behavior versus the temperature.
Dry sample, the value of the conductivity is negligible because only some confined particles of water remain in the sample.

Moreover, depending on the frequency a susceptibility of the liquid and the solid parts of the leaf is detected at high and low frequencies respectively (Fig. 4), this sensitivity allows to quantify the amount of water stored in the plant leaf according to the variation of the relaxation peak with respect to a reference measurement.

At very high frequency (1 MHz), the dielectric response of the liquid part is too sensitive, this is shown at -13 °C which is less than the usual temperature of transition (0 °C), however the second sensitivity is shown well for low frequency and for 73 °C. This negative change in temperature is due to the fact that water molecules are not completely free, they are connected to the components of the leaf which induces chemical interactions under the effect of increasing temperature.

This result confirms the modeling proposal of the leaf, where it is simply considered as a composite of liquid and solid matter. The liquid is fully susceptible to very high frequency while the sensitivity of the solid part is greater at low frequency which is advantageous for the study of the pyrolysis process and ignition.

Furthermore, and depending on the temperature the relaxation frequency is shifted in two main directions (Fig. 5), it increases considerably with the temperature up to 20 °C, and then decreases towards the low frequency. This shift towards high frequency is due to the existence of a considerable amount of water in the leaf in the ice-liquid phase transition, but the shift to the low frequency characterizes the release of the different components of the leaf starting by the water molecules (evaporation) to the ignition (solid-gas phase transition). The latter is not completely shown because the analyzer does not scan the low frequency (Fig. 6). These offsets are spontaneously separated by a stabilization of 15 °C around the ambient temperature.
This dependence on the frequency and on the temperature defines a new characteristic variable of the phase transition that is the activation energy of the transition. So, each transition is characterized by an energy $E_a$ given by:

$$f \approx f_0 e^{-E_a / KT} \Rightarrow E_a = -KT \ln \left( \frac{f}{f_0} \right)$$

This energy is the threshold for a transition from one phase to another, so the activation energy of the ice-liquid is determined in the range of temperature from -50 to 15 °C and it is around 1.21 eV (Fig. 7A). However, above 60 °C, this value is not unique due to the emission of several components at the same time or successively (Fig. 7B).

The characterization of this behavior is mentioned in the following paragraph with the exposition of the TGA/DTA results.
The obtained results show the appearance of a high endothermic peak in the DTA curves between 50 and 118 °C corresponding to the evaporation of the water contained in the leaf (Fig. 8a). This loss presents nearly 40% of the total sample weight in the fresh case against only 10% in the dry case (TGA curve, Fig. 8b).

![Diagram](image1.png)

**Fig. 7** Transition line during the temperature field (A) Ice/Liquid (B) liquid & solid/gas.

![Diagram](image2.png)

**Fig. 8** TGA/ADT curve of a Laurel leave fresh and dry sample. The inset in the Heat Flow graph is a zoom of the dry sample flux between 100 °C and 200 °C.

Afterwards, between 120 °C and 155 °C a slight increase was seen for the fresh sample while it is notable for the dry sample (inset Fig. 8a), this reaction is due to the beginning of the decomposition of the aromatic compounds of the Laurel leaf (cycle opening of cineole, lactone C5). Furthermore, this latter transformation does not modify the sample weight.
However, around 180 °C, these aromatic elements are released as well as the terpenoids which reduces the sample weight until reaching the temperature of 250 °C (Fig. 8b). This is the hemicelluloses decomposition which issues a small quantity of volatile compounds such as CO, CO₂ and OH.

This reaction is well illustrated in the DTA curves of the dry sample because of the concentration of the aromas that increases significantly with the degree of drying of the laurel leaves. This is reflected in the inequality of the weight loss rate between the dry (~37%) and the fresh sample (~22%) as shown in Fig. 8b.

Thereafter, a two successive peaks is observed, which appear well in the curves HF-1 (Fig. 9), the first is between 384 °C and 464 °C, due to the release of the lauric acid that causes hazardous and toxic smoke and irritation to the eyes. Beside that there is also the release of sesquiterpene lactones which induce major allergenic risk.

At this stage, the weight loss is significant and continues to the end of the second peak about 570 °C (Fig. 8b), which identifies the breakdown of cellulose (384 °C-464 °C) and lignin (464 °C-576 °C) successively, wherein during this process the greatest amount of volatile components is released, such as CO, CO₂, H₂ and CH₄.

Beyond this stage the sample weight stabilizes which define the end of ignition because then only the ash exists (Fig. 8b).

5. Conclusions

The dielectric response shows the existence of a relaxation frequency at each level of temperature; the behavior of this specific value regarding the temperature and frequency describes the sensitivity of the leaf to the water lost. Furthermore, the TGA/DTA confirm the results of the dielectric spectroscopy for the evaporation phase and complete the characterization until the ignition which was not possible with the dielectric technique due the limited frequency range of the analyzer.

Moreover, regarding the TGA/DTA tests the pyrolysis process is fully described with exposing the total reaction and the released elements that occurred in the cell under high temperature increase, this characterization shows the existence of a set of dangerous and toxic elements that make the fight against fire hard without special equipment such as eyes and face and respiratory protection, gloves and protective clothes.

Finally, it is expected to extend this study for several types and species of plants and for different heating rate in order to analyze the behaviour of ignition energy and time of combustion to create a data base of all this information to predict fire spread with a comparable network to a real forest.

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