

ATR investigation of the mass residue from the pyrolysis of fire retarded lignocellulosic materials

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ABSTRACT

The objective of this study was firstly to assess the magnitude of the chemical effect of DAP as fire retardant on the lignocellulosic material *Olea europaea* employing TGA. Therefore pyrolysis experiments of *O. europaea* before and after treatment with DAP 15% have been conducted using a TGA analyzer under nitrogen (N₂) flow. Secondly the objective was to investigate the effect of DAP at different temperatures based on the solid mass residue using infrared spectroscopy. Thus, mass residues obtained at 180, 260, 320, 400, 500 and 600 °C respectively from TGA were examined by FTIR-ATR. Using the TGA curves of DAP and *O. europaea* (pristine) respectively, a calculated curve has arisen ($0.85 \times \text{TG curve}_{O. europaea}^{25-500^\circ\text{C}} + 0.15 \times \text{TG curve}_{\text{DAP}}^{25-500^\circ\text{C}}$). A comparison between this curve and the measured of the sample *O. europaea* + DAP 15%, showed that since they do not coincide, there is a chemical synergy between *O. europaea* and DAP. FTIR-ATR was employed to investigate the decomposition path of hemicelluloses, cellulose and lignin by detecting the characteristic peaks of the pyrolysis mass residues at different temperatures. Above 25 °C, several characteristic peaks gradually do not reappear. On the contrary, when DAP is present these characteristic peaks continue to appear shifting to higher temperatures implying its chemical effect on the lignocellulosic materials. This observation is verified by the shifting of the DTG curve of *O. europaea* treated with DAP towards lower temperatures and less pronounced peaks at the DTG curves. The combination of TGA and FTIR-ATR is a useful tool for the investigation of a fire retardant's effect on the thermal decomposition of lignocellulosic materials.

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1. Introduction

The terms forest fires or wildfires are often used to signify an uncontrolled intense fire that breaks out in the wooded areas due to many factors ranging from natural to man-made causes. The ecological consequences are vast, as they degrade the fauna and destroy the biodiversity, especially in dry climates such as in the Mediterranean countries. The huge expenses needed to extinguish fires and restore the damages, the burning of timber and other forestry products, the loss of crops etc., render wildfires a huge economical problem.

Therefore, it is crucial that the forest fires are encountered. For their suppression, fire retardants play an important role. Fire retardants are defined as chemical compounds that modify pyrolysis reactions of polymers (natural like wood etc. or synthetic) or

oxidation reactions implied in the combustion by slowing down or by inhibiting them. They are classified as long-term (chemical) or short-term (suppressants) retardants. Long-term retardants are applied ahead of a wide fire front to reduce the rate of fire spread or the intensity. They consist of flame inhibiting chemicals dissolved in water. They remain effective even after water has evaporated. The essential ingredient in these retardants, which alter the pyrolysis mechanism, is the active fire retardant substance, usually referred as 'active salt', which is typically either an ammonium phosphate (i.e. (NH₄)₂HPO₄ or DAP) or ammonium sulfate (i.e. (NH₄)₂SO₄ or AS). DAP and AS are producing an acid (phosphoric or sulfuric) prior to the ignition temperatures which alters the decomposition path of the forest fuel and leads at high dehydration of the lignocellulosic matrix. The result is the increased quantities of char, water vapor, CO₂ and the reduction of the volatile products [1].

Several theories have been proposed for the mechanism of fire retardancy [2]. These are: (1) barrier theory (the retardant insulates the forest species preventing oxygen reaching the fuel); (2) thermal theory (heat is absorbed by the retardants preventing forest fuel from igniting); (3) non-combustible gases theory (the retardant is

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decomposed to non-flammable gases, i.e. H_2O); (4) free radical trap theory (formation of free radicals which inhibit the chain propagation mechanism of combustion); (5) increased char/reduced volatiles theory (the retardant lowers the temperature at which pyrolysis occurs, directing the degradation pathway towards more char production and fewer volatiles).

Specifically as far it concerns the last mechanism, a fire retardant can cause the formation of a carbonized layer at the surface of the polymer by chemical transformation of the degrading polymer chains. The physical structure of char acts as an insulating layer between the gas phase and the condensed phase which isolates and protects the polymer from the flames. It limits the volatilization of fuel and prevents the formation of new free-radicals. It also limits oxygen diffusion, which reduces combustion. Lastly, it insulates the polymer underneath from the heat [3]. The char itself can undergo glowing combustion when it is exposed to air. However, it is unlikely that both glowing combustion of the char and significant gas-phase combustion can occur in the same zone above the surface, since the flow of volatiles through the char will tend to exclude air from direct contact with the char. Therefore, generally, solid-phase char combustion tends to occur after volatilization has largely ended [4].

Thermal analysis is probably one of the most useful microscale analytical methods that can be applied to investigate the chemical mechanism of fire retardants [5–9]. There are several reasons why the relevance of thermoanalytical studies to fire performance can be questioned: heating rates, amount of material and lack of heat feedback are the major ones [4]. However, these studies do give important information about the decomposition process. TGA gives the onset and the endset temperatures, the inflection point (the temperature at which maximum mass loss rate occurs) and the mass residue, directly. It also gives with calculation through kinetics the activation energy and the pre exponential factor. SDTA directly gives the ignition temperature. Lastly, DSC directly gives the heat of melting and with calculation the heat of pyrolysis and the specific heat. Thermal analysis has also the advantage to be combined with other analytical techniques [10] like GC–FTIR [11], FTIR–ATR [12], MS [13] and cone calorimeter [14].

Especially, TGA has been proved a very useful tool because the heating rate and the conditions under which an experiment takes place are extremely well-controlled. The environment of thermal decomposition can be altered, varying from pyrolysis (nitrogen flow) to combustion. Pyrolysis is a thermochemical decomposition taking place without the presence of oxygen and it involves simultaneous changes of chemical and physical phases. It is an endothermic process as it needs energy to take in, in order a material to decompose. Pyrolysis produces gas and liquid products and leaves behind a solid residue, rich in carbon content (char).

The aim of this work was to assess the magnitude of the chemical effect of DAP on a forest fuel, employing TGA and further to investigate DAP's effect at various temperatures based on the mass residue, employing FTIR–ATR.

2. Experimental

2.1. Materials

Olea europaea is a drought tolerant forest species thus very common in regions where dry climates prevail like Mediterranean. Such regions are vulnerable to wildfires and frequently devastated by them.

The fire retardant used was the inorganic salt $(NH_4)_2HPO_4$ (DAP). This salt has prominent use as fire retardant since the early 1960s, because of its intrinsic effectiveness and its common use

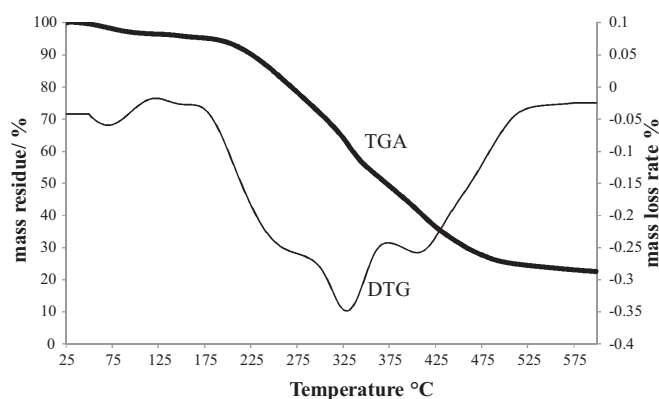


Fig. 1. TGA and DTG curves of *Olea europaea* in nitrogen (N_2) atmosphere at heating rate $10\text{ }^\circ\text{C min}^{-1}$.

as agricultural fertilizers. This has assured its abundance, relative cheapness and environmental compatibility [1]. DAP alters the pyrolysis of forest species, usually by acid catalyzed dehydration reactions. Thus, it promotes the formation of H_2O , CO_2 and char, at the expense of volatile products [15]. It also increases considerably the ignition delay time and the pyrolysis mass residue [6].

2.2. Methods

2.2.1. Thermogravimetric (TGA) analysis

Thermogravimetry (TGA) was carried out using a Mettler Toledo TGA/SDTA 851 apparatus, with temperature accuracy and temperature reproducibility of $\pm 0.5\text{ }^\circ\text{C}$. The samples, approximately 20 mg in weight, were introduced into an open alumina crucible (Al_2O_3) of 150 μl . They were heated from $25\text{ }^\circ\text{C}$ up to $600\text{ }^\circ\text{C}$ with a linear heating rate of $10\text{ }^\circ\text{C min}^{-1}$ and at a flow rate of 50 ml/min in nitrogen atmosphere. In order to get the ATR samples, following the same procedure, runs have been conducted from $25\text{ }^\circ\text{C}$ up to 180, 260, 320, 400, 500 and $600\text{ }^\circ\text{C}$ respectively.

2.2.2. Attenuated total reflection infrared (FTIR–ATR) analysis of solid residues

FTIR–ATR analyses were carried out on a Jasco FT-IR 4200 ATR PRO 410-S spectrometer, in the range $700\text{--}2700\text{ cm}^{-1}$ with a resolution 4 cm^{-1} . ATR spectra were obtained from *O. europaea* before and after treatment with DAP at $25\text{ }^\circ\text{C}$. The respective pyrolysis mass residues which were collected at different stages of thermal decomposition in the TGA at 180, 260, 320, 400, 500 and $600\text{ }^\circ\text{C}$, were kept in a desiccator under nitrogen atmosphere, until the sample reached the room temperature. Once the sample did so, the ATR experiments were initiated.

3. Results and discussion

3.1. Thermal analysis

The results of thermogravimetric analysis for *O. europaea* before and after treatment with DAP 15%, are expressed by the TGA curves and their derivatives (DTG) (Figs. 1–3).

Based on the DTG curve of *O. europaea*, four different regions in which considerable weight losses take place are distinct. The first is $<125\text{ }^\circ\text{C}$ and corresponds to the evaporation of moisture. The region around $175\text{--}290\text{ }^\circ\text{C}$ corresponds mainly to hemicelluloses decomposition, while the next one around $290\text{--}375\text{ }^\circ\text{C}$ to cellulose decomposition. The last region around $375\text{--}525\text{ }^\circ\text{C}$ is related to the lignin decomposition [16]. It has been observed that in forest species with such a thermal degradation (comprising of more than

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