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THE EFFECT OF FIRESORB AS A FIRE RETARDANT ON THE THERMAL PROPERTIES OF A HEATED SOIL

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The DSC technique was used to characterise under laboratory conditions, the effect of a polymer substance, Firesorb, that tries to be used as a flame retardant in forest fires, over two different Galician soils (NW Spain). Samples of these soils with different doses of this retardant were heated in an oven at 230 and 350°C to simulate medium and high intensity fires, respectively. The effect of the retardant was determined as a result of the comparison between the enthalpy of combustion of the organic matter and the ignition temperature of these subsamples and the corresponding unheated and untreated ones. Both parameters, enthalpy of combustion and ignition temperature, were determined directly from the DSC experiments. The results showed that the effect of the retardant remains clear in heating at 230°C and the content of organic matter of the soil was a determining factor in its quantification. However the effect of the retardant in heating at high temperatures is almost null in both soils.

Keywords: *DSC, firesorb, forest fire, organic matter, retardant*

Introduction

Galicia, (NW Spain) is one of the most affected regions by forest wildfires in Europe, where, not only thousands of forest hectares have been devastated in the last years, but several human lives have also been lost. Likewise, the combustion of the organic matter, that takes place during the fires, throws out to the atmosphere a great quantity of carbon dioxide, which is one of the causative gases of the greenhouse effect. According to the criteria of the Kyoto protocol, a global reduction of these emissions is necessary, particularly in the Galician region, where the emissions have been increased due mainly to forest fires.

The extent and duration of the effects of fires on soils, water and air depend firstly on fire severity, which in turn, is controlled by several environmental factors that affect the combustion process, such as, amount, nature and moisture of live and dead fuels, air temperature and humidity, wind speed and topography of the land site when the fire starts. Fire severity depends also on intensity and duration, and the intensity is directly related with the temperature raised during the fire [1].

To minimize the number of fires and the effects that they produce in human lives and the environment is a task of basic importance. In this way, several types of chemical agents grouped into two categories, retardants and foams, gain acceptance as effective tools for wildfire fighting [2–5]. The retardants are a mixture of chemical agents that make the water denser and turn fuels less flammable and are normally applied in the front of an advancing fire or along its flanks to reduce intensity and ability to spread, and their effectiveness could depend on the amount of retardant applied per unit surface area. Firesorb is an acrylic polymer used recently in this region as a fire-extinguishing agent [3, 6].

The calorimetric techniques are very useful for soil and its components studies, as the increasing number of references in the last two decades indicate [7–10]. Concretely DSC, which is a physico-chemical technique based on computer-controlled heating of the sample in a controlled atmosphere, could give information about the characteristics of the organic matter from the shape, size and position of the peaks which the DSC curve shows when the soil sample is heated. Indirectly, from these data it is possible to quantify the effects of the fire on the soils [8]. In this sense, this technique has demonstrated to be easy, rapid and convenient tool for the characterization of soils, and, in addition, small amounts of samples required could be an advantage when only a small representative sample is available.

Using the DSC technique, the effect of the concentration of the retardant Firesorb on the organic matter of a soil has been examined in this work in soils heated under laboratory conditions at different temperatures to simulate high and medium intensity fires. It is very useful to heat the soil under controlled

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laboratory conditions in order to contribute to the better knowledge of the effects of heating at given temperatures on the soil organic matter, due to the great quantity of variables that influence on these effects [11].

From DSC curves of sample soils, made after the heating, the enthalpy of combustion of the organic matter and the ignition temperature [12, 13] were obtained and used to quantify the effect of the retardant by comparison with the same parameters obtained in unheated and untreated soil samples.

Experimental

Materials and methods

Two Galician forest soils (NW Spain), Humic Cambisol over granite were selected for this study. These soils which are representative of the main forest ecosystems affected by wildfires in Galicia were located at Monte Pedroso (Begonte, province of Lugo) and Monte Nigoi (A Estrada, province of Pontevedra) and were sampled from the top (0–2 cm depth) of the A horizon. The soil samples were dried, sieved 2 mm and ground at the laboratory.

Firesorb is a polymer substance made of acrylic acid compounds, water, oil phase and emulsifiers, supplied by Stockhausen (Degussa-Hüls Gruppe, Germany) which is being tested as a fire fighting chemical agent in Spain [3, 14].

Twelve subsamples of every soil were prepared and divided in four groups of three: non-treated samples, samples treated with a watery solution of Firesorb at 1.5% with a dose of 20 g m^{-2} (low dose), samples treated with a watery solution of Firesorb with a dose of 30 g m^{-2} (medium dose) and samples treated with a watery solution of Firesorb with a dose of 50 g m^{-2} (high dose). The medium dose, which is recommended by suppliers, corresponds with the normal levels of application under field conditions, but low and high retardant concentrations can be occasionally found in some soil areas due to the irregular or repeated application of the product.

One soil sample of each group was heated in an oven at 230°C, another at 350°C, simulating medium and high intensity wildfires, respectively, and one soil sample of each group remaining without heating. In order to avoid important temperature gradients into the sample during the heating, the sample thickness was 2 cm.

Due to the fact that the programmed temperature was similar (230°C) or greater (350°C) to the ignition temperature of the Galician natural soil (220–230°C) [13], the combustion could take place inside the oven, liberating a great quantity of heat. Consequently, the temperature of the sample, which is controlled by a thermocouple located on the sample, was superior to the programmed one. After reaching the selected heating temperature, the soil samples were maintained 15 min inside the oven at constant temperature. Afterwards they were withdrawn and kept at room temperature.

DSC curves of the burnt and unburnt soil samples were carried out using a Differential Scanning Calorimeter (DSC-2910 TA-Instruments) and replicated six times. All DSC curves showed a scanning between 50 and 600°C at 10°C min^{-1} of a soil sample among 10 and 30 mg placed in an open aluminium pan, under a dry air flowing of 110 cm^3 min^{-1}.

The enthalpy of combustion and the ignition temperature of the soil organic matter, calculated directly from the DSC curves, as exposed in previous works [8], are directly related with the organic matter content and its composition, and provide us with information about the thermal potential degradation of the soil. The heating of the soil in the oven provokes important changes in these thermal properties, which can then be used as indicators of the heating impact and hence as indicators of the effect of the Firesorb.

To compare the obtained results, the t-Student test with a 95% probability level was applied, using the computer program SPSS 11.5.

Results and discussion

Unheated soils

Figure 1 shows a comparison between the DSC curves of unheated samples of Monte Pedroso and Monte Nigoi soils. Both present three peaks with different origins: the first one, endothermic, is due to dehydration and loss of volatile substances and

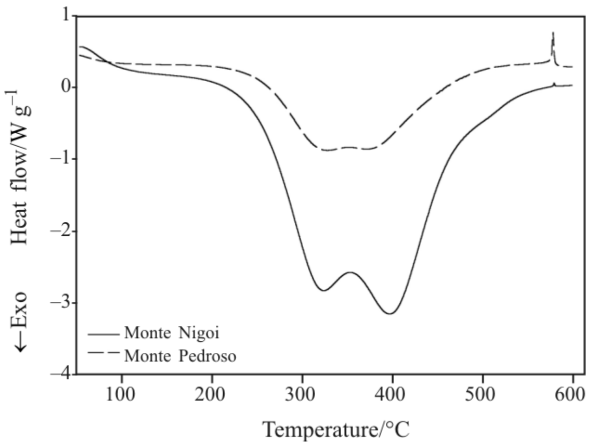

Fig. 1 Comparison between the DSC curves of unheated Monte Nigoi and Monte Pedroso soils

appears up to 50°C; the second peak, exothermic, appears between 220 and 575°C and is due to the combustion and degradation of the organic matter of the soil. This peak can be considered as the overlapping of two exothermic reactions from the decomposition and combustion of different organic matter components, with distinct and contrasting thermal stability [15, 16]. The first one presents a minimum between 300 and 340°C attributed to decomposition of more thermolabile compounds, basically aliphatic compounds, such as cellulose, holocellulose, fulvic acid and simple sugars; whereas the second one presents the minimum between 370 and 400°C, due to decomposition of less thermolabile material, mainly aromatic components, such as humic acids and lignin [17, 18]. Satoh called those peaks LER and HER, abbreviations of lower and higher temperature reactions [15]. The last peak, endothermic, which appears at approximately 575°C, was attributed to the polymorphic transformation of hypothermic quartz to hyperthermic quartz that starts at this temperature [8] and it is more visible in the DSC curves of the soils with minor organic matter content, as in the case of Monte Pedroso soil (Fig. 1).

Table 1 shows the combustion enthalpy of the organic matter of soil heated and unheated samples with and without Firesorb.

No statistically significant differences with the dose of retardant have been found in both unheated soils. The LER peak is smaller than the HER peak, representing the heat released during the combustion of organic matter associated to the HER peak between 58 and 60% of the total heat, therefore, the aliphatic components, which are the least thermal stable, are in minor proportion than the aromatics in both soils.

Table 2 shows the ignition temperature of all the soil samples, untreated, treated with different doses, heated and unheated in both soils. A light increase on the ignition temperature with the amount of retardant was found in the unheated samples of Monte Pedroso and Monte Nigoi soils. In this way, one of the immediate effects of this retardant could be a delay in the ignition process, i.e. the soil needs to raise higher temperature (and then, more heat contribution) to start the combustion of the organic matter, particularly in Monte Pedroso soil.

Heated soils

The temperature raised by the sample during the heating was always higher than the temperature programmed in the oven. That was due, as it was noted above, to the fact that the combustion of organic matter took place and the heat released provokes an increment in the temperature of the sample between 20 and 30°C with respect to the programmed temperature. On the other hand, as first effect, it has been observed, that the necessary time to reach the oven programmed temperature was higher in soil samples that have been treated previously with retardant. The values are not presented in this work.

The enthalpy of combustion of the organic matter of the heated soils is lower than the corresponding non heated soil, due to the destruction of a part of the organic matter during the heating. Figure 2 shows, as an example, the overlapping of DSC curves

Table 1 Combustion enthalpy values of the whole organic matter (ΔH), in kJ/g, for Monte Pedroso and Monte Nigoi soils with regard to the temperature of heating and the dose of retardant added

Dose	Unheated		Heated at 230°C		Heated at 350°C	
	Monte Pedroso	Monte Nigoi	Monte Pedroso	Monte Nigoi	Monte Pedroso	Monte Nigoi
Not treated	0.71±0.03	3.3±0.1	0.36±0.06	2.3±0.1	$(20\pm3)\cdot10^{-3}$	0.40±0.02
Dose 1	0.73±0.01	3.1±0.2	0.46±0.03	2.3±0.1	$(37\pm1)\cdot10^{-3}$	0.33±0.01
Dose 2	0.71±0.03	3.2±0.1	0.48±0.02	2.9±0.1	$(43\pm3)\cdot10^{-3}$	0.62±0.06
Dose 3	0.72±0.01	3.4±0.1	0.53±0.05	2.7±0.1	$(20\pm1)\cdot10^{-3}$	0.31±0.01

Table 2 Ignition temperature (T_{ign}) in °C for the Monte Pedroso and Monte Nigoi soils with regard to the temperature of heating and the dose of retardant added

Dose	Unheated		Heated at 230°C		Heated at 350°C	
	Monte Pedroso	Monte Nigoi	Monte Pedroso	Monte Nigoi	Monte Pedroso	Monte Nigoi
Not treated	239±10	246±12	326±17	327±12	405±12	382±15
Dose 1	242±11	247±10	285±13	297±11	392±12	388±23
Dose 2	245±9	247±10	264±9	277±10	388±10	375±20
Dose 3	247±11	249±11	263±9	300±17	396±17	394±21

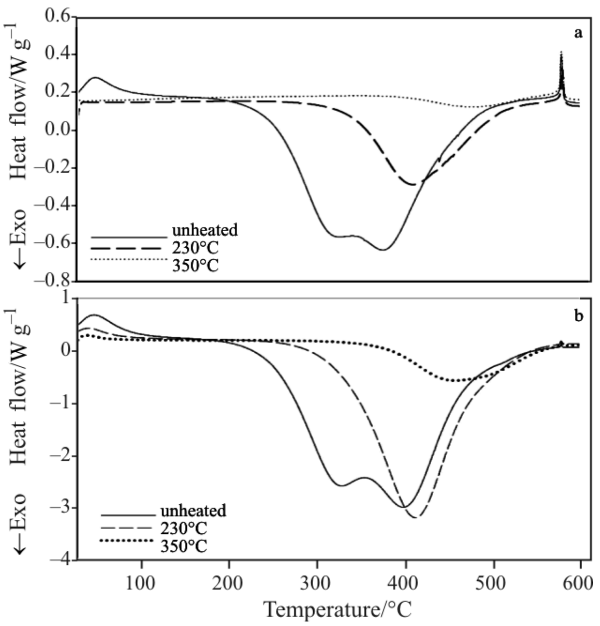

Fig. 2 Comparison between the DSC curves of the unheated, heated at 230°C, heated at 350°C soils samples without retardant of a – Monte Pedroso and b – Monte Nigoi

of the unheated soil, soil heated at 230°C and soil heated at 350°C of Monte Pedroso and Monte Nigoi soils without retardant. The area of combustion peak decreases with the heating temperature in both soils, being very small in samples heated at 350°C. The values of enthalpy of organic matter (Table 1) ratified these previous observations, indicating a moderate decrease of organic matter at 230°C whereas at 350°C the combustion of organic matter was practically completed, these findings agreeing with those of several authors [11, 19, 20].

The organic matter loss as a consequence of the heating can be calculated from the comparison of the combustion enthalpy of organic matter of heated and unheated samples [8]. The results are shown in Table 3.

Table 3 Loss of organic matter for the Monte Pedroso and Monte Nigoi soils with regard to the temperature of heating and the dose of retardant added

	Heated at 230°C		Heated at 350°C	
	Monte Pedroso	Monte Nigoi	Monte Pedroso	Monte Nigoi
Not treated	49	30	97	88
Dose 1	37	26	95	89
Dose 2	33	10	94	81
Dose 3	26	20	97	90

The loss of organic matter was lower in Monte Nigoi soil, in all cases. That fact indicates that the heating impact depends strongly on the nature of the soil and having in mind that both soils have similar characteristics, the organic matter content is the factor with the maximum influence on the heating effects. The addition of retardant implied an important decrease in the loss of organic matter in heating at 230°C, whereas no significant differences with the dose have been found in heating at 350°C in this parameter.

In order to carry out a clear comparative analysis, Fig. 3 shows the overlapping of the DSC curves of unheated, heated at 230°C and heated at 350°C samples treated previously with the three different doses of Firesorb, and the untreated samples of both soils. DSC curves of samples heated at 230°C are characterised by an important reduction of the LER peak, the more thermal resistant peak (HER peak) remaining in both soils. But a nearly complete

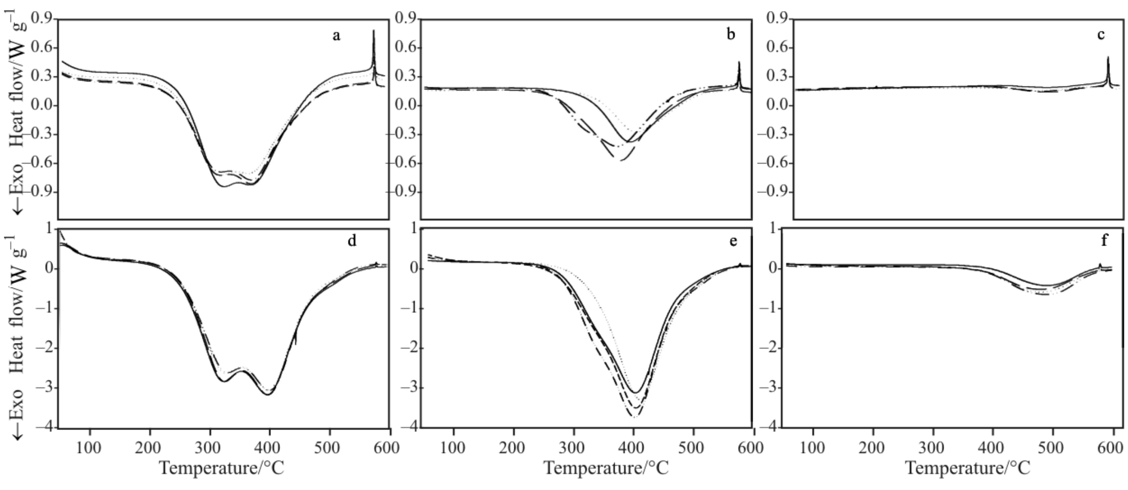

Fig. 3 Comparison between the DSC curves of Monte Pedroso soil a – unheated, b – heated at 230°C, c – heated at 350°C and Monte Nigoi soil d – unheated, e – heated at 230°C, f – heated at 350°C with different treatments: ···· – non treated, – – – – high dose, –··–··– – medium dose and —– – low dose

reduction in both peaks has been found in samples heated at 350°C, particularly noted in Monte Pedroso soil, which presents around 95% of reduction of the organic matter in all the treatments. Significant differences have been found between the enthalpy of combustion of treated and untreated samples heated at 230°C in both soils, the lowest values corresponding to untreated samples, revealing that the addition of Firesorb reduces the impact of fires on soil, in spite of the fact that the effectiveness of the retardant decreases with the temperature of heating.

DSC curves of samples of Monte Pedroso soil heated at 230°C showed an almost complete disappearance of LER peak in all of the treatments. However after the comparison of enthalpy of combustion of organic matter between heated and unheated samples, only the sample untreated and heated at this temperature, caused a complete elimination of the LER peak, even a mean reduction of approximately 15% of the HER peak, whereas the treated samples preserve HER peak intact. Monte Nigoi soil does not present a complete reduction of LER in any case at this temperature, notwithstanding it is very complicated to observe this peak in the DSC curves, appearing rather as a shoulder. Significant differences on the enthalpy of combustion can be observed in samples treated with medium and high dose against untreated and treated with low dose. After the comparison of this parameter with unheated soil it was observed that LER peak presented an important reduction, as it had been expected, of 85 and 75% in samples untreated and treated with low dose respectively, whereas the results corresponding to medium and high dose retardant were 55 and 60%.

These facts assure that besides the addition of retardant, the content of organic matter is a determinant factor in the mitigation of the impact of heating corresponding to medium intensity fire.

DSC curves of samples of Monte Pedroso and Monte Nigoi soils heated at 350°C with and without different amounts of retardants, showed a small peak HER, which is practically coincident with the baseline of the DSC in Monte Pedroso soil (Fig. 1). In spite of the fact that the data of enthalpy of combustion of organic matter are very different between both soils, the loss of organic matter calculated from these data was rather similar for both soils (Table 3). Therefore the organic matter has practically disappeared and the effect of heating at high temperatures is too great in order to consider the possible recovery of soil, independently if they have been treated with retardant or not.

The ignition temperature of the soil samples heated at 230°C is, in both soils, higher than unheated samples, as it was observed in soils from this region affected by wildfires [13]. The major values were in the samples without retardant and the lowest values were the corresponding to medium and high doses. Though the impact on the soil is visible in all the samples burned to 230°C, the thermal degradation during the heating has been lower in the soils treated with the retardant.

A great increase in the ignition temperature of the samples heated at 350°C was observed, obtaining values close to 400°C in all the samples and no significant differences have been found with the dose of retardant in any case. When heating at high temperatures, the effect of Firesorb is almost nonexistent, the most remarkable effect is, as was mentioned above, that the treated samples needed more time to raise the temperature in the oven.

Conclusions

Calorimetric technology is a very useful and profitable tool for the rapid evaluation of possible impacts on soil and of the possible actuations that can mitigate them, for example the addition of retardant in order to minimise the fire effects. In this way the main results of this work are the following:

- The addition of Firesorb provokes a delay in the ignition temperature of unheated soils, thus becoming more resistant to thermal degradations.
- The addition of retardant diminishes the organic matter lost as a consequence of the heating.
- The effect of Firesorb remains clear in heating associated to medium temperature fires and despite the fact that the soils are maintained during enough time in the oven after having reached the programmed temperature; the impact is lower in soils with high organic matter content.
- The effect of the retardant is practically undetectable at high temperature heating.
- Firesorb can be used in forest ecosystems to control wildland fires and prescribed burns, but only after evaluating its impacts on the environment.

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