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Fire retardancy impact of sodium bicarbonate on ligno-cellulosic materials

D. Bakirtzis[a,*], M.A. Delichatsios[a], S. Liodakis[b], W. Ahmed[c]

[a] *Fire Dynamics and Materials Lab., Fire Safety Engineering Research & Technology Centre (FireSERT), School of the Built Environment, University of Ulster, Jordanstown campus, Shore Road Newtownabbey, Co. Antrim, BT37 0QB Belfast, Northern Ireland, UK*
[b] *Laboratory of Inorganic and Analytical Chemistry, School of Chemical Engineering, National Technical University of Athens (NTUA), 9 Iroon Polytecniou Street, Athens 157 73, Greece*
[c] *Center of Nanotechnology & Advanced Manufacturing, University of Central Lancashire, School of Computing, Engineering and Physical Sciences, Preston PR1 2HE, UK*

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ABSTRACT

In this paper, the effect of $NaHCO_3$ as fire retardant additive during pyrolysis and combustion has been investigated. Four different contents (5%, 10%, 15%, and 20% w/w) of $NaHCO_3$ have been tested on *Pinus brutia*, *Laurus nobilis* and *Nerium oleander*; forest species commonly dispersed in the Mediterranean region. Pyrolysis experiments have been conducted using a thermogravimetric analyzer (TGA) employing nitrogen (N_2) flow of 50 ml/min, under a heating rate of 10 °C/min. Experiments for flaming combustion have been conducted in a specially designed furnace, isothermally controlled, under an air flow supply of $1.5\,l\,min^{-1}$; key parameters including time to self ignition and duration of flame combustion were measured. Pyrolysis data revealed that the addition of $NaHCO_3$ induces a shift towards lower thermal degradation temperatures for each of the forest specie considered. Thus, sodium bicarbonate decreases the threshold of initial temperature of pyrolysis of forest species (promotion effect). On the other hand $NaHCO_3$ increases the self ignition delay time and combustion duration of forest species (inhibition effect). In addition the presence of $NaHCO_3$ increases the pyrolysis mass residue of forest species, especially when sodium carbonate applied on *N. oleander*.

1. Introduction

Forest fires have devastating effects on large areas every year causing heavy material damage, loss of animal and human lives. Wild land fires overload the ecosystem, degrade the fauna and destroy the biodiversity [1] especially in dry climates such as in the Mediterranean countries [2]. The protection of the forest regions is becoming a high priority owing to progressive climate change and drought. Prevention is one of the best ways of combating forest fires by using various techniques such as firebreaks, minimum separation distances between housing and forest areas, collection of residual forest biomass and controlled burning [3].

Natural cause fires start either by spontaneous or by piloted ignition of dry fuel especially in hot and dry climates. Lighting is a possible common cause for self ignition Forest fires in remote areas can burn for hours becoming severe and difficult to extinguish before being detected by fire fighting authorities. Fires detected in early stages are much easier to extinguish.

In fire fighting, fire retardants play an important role [4]. Fire retardants are classified as long-term (chemical) or short-term (suppressants) retardants. Long-term fire retardants are applied ahead of a wide fire front to reduce the rate of fire spread or the intensity.

Sodium bicarbonate ($NaHCO_3$) is considered to be one the most effective fire retardants producing carbon dioxide (CO_2) and water (H_2O) when it is heated [5]. The thermal decomposition of sodium bicarbonate can be represented by a multi step mechanisms [6,7]. The overall global decomposition is given by the following steps:

$$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(l) \quad \text{(a)}$$

The sodium carbonate decomposes into sodium oxide and carbon dioxide.

$$Na_2CO_3(s) \rightarrow Na_2O(s) + CO_2(g) \quad \text{(b)}$$

The sodium oxide reacts with water vapor to form an alkaline sodium hydroxide which could interact with the homogeneous chemistry of the flame.

$$Na_2O(s) + H_2O(g) \rightarrow 2NaOH(s) \quad \text{(c)}$$

Even though the exact mechanisms are not well established, the NaOH formed may promote catalytic recombination of the radical species needed for flame propagation, causing the flames to extinguish.

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[*] Corresponding author. Tel.: +44 28 90368083; fax: +44 28 90368726.
E-mail addresses: d.bakirtzis@ulster.ac.uk, aseviros@hotmail.com (D. Bakirtzis).

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$NaHCO_3$ has been tested as an additive in forest species which are composed of three primary components, namely hemicelluloses, cellulose and lignin in proportions related to the particular specie [8]. The pyrolysis of the forest species can be considered as the pyrolysis of a composite fuel made out of these three components. Simultaneous TGA and DTA for the thermal of degradation of wood products is used very often [9].

In general we can say with no doubt that Thermal Analysis is a significant method for studying the thermal decomposition of lignocellulosic materials. Data derived from TA is important for wild land fires modelling purposes [10]. Modelling required parameters for forest species, such as specific heat and enthalpy of vaporization can be calculated with the instantaneous weight loss to subtract the heat flow corresponding to this component from the DSC baseline [11]. Also, the heating value of volatiles released from a forest fuel during pyrolysis can be determined as a function of time and it can be calculated with the use of TA. The relation between temperature change and heat release value can be given by the convolution integral of the DSC curve [12].

Self-ignition occurs when the sample temperature reaches a certain temperature – known as the ignition temperature – and combustion initiates flammable vapor air mixtures in the vicinity of the surface. The flammable vapor-air gas mixture is the product of the thermal degradation of hemicelluloses and cellulose. The time to self-ignition temperature depends on many factors including the material, the shape, the size, the sample mass and the density of the samples [13].

Combustion is an exothermic process, self sustaining reaction, involving a fuel in the form of a solid, liquid and/or gas. The proportional composition of the three main components: hemi-cellulose, cellulose and lignin, vary for each forest species. Higher cellulose and lignin content is leading to better thermal stability of the wood in different temperature regimes [14]. In this paper the effects of sodium bicarbonate on fire retardancy during pyrolysis and combustion on various forest species have been investigated. Three forest species were tested using different concentrations of sodium bicarbonate. Pyrolysis study has been investigated using TGA under nitrogen flow, whereas self-ignition and combustion have been investigated using a custom designed apparatus.

2. Experimental

2.1. Methods

2.1.1. Thermogravimetric analysis

The pyrolysis experiments were carried out using a Mettler Toledo TGA/SDTA851^e measuring module, with temperature accuracy of ±0.5 °C and temperature reproducibility of ±0.3 °C. The samples were placed in an alumina (Al_2O_3) pan (with no lid) of 70 μl volume capacity and heated under a dynamic linear rate of 10 °C/min, in 50 ml/min nitrogen (N_2) flow, from 25 °C to 700 °C. All samples weighted approximately 10 mg (±1 mg). Owing to the small sample mass size the temperature of the sample was uniform and the interpretation of results was less unambiguous.

Lignocellulosic materials are natural polymers presenting a complex structure. Hence, it is difficult to separate the individual components in an economic manner. Pyrolysis is important for the investigation of the primary and secondary reactions, as it involves the degradation of macromolecular material with heat alone in the absence of oxygen. The solid residue product of the thermal degradation derives by dehydration and condensation reactions. These are known as recondensed materials [15]. The chemical composition of each type of wood or forest specie together with the compounds added for each application like fire retardancy, play a fundamental role in the kinetic behavior of their thermal decomposition [16]. For the kinetic study of forest species, a two-stage semi-global kinetic model consisting of four sequential steps is frequently proposed to derive parameters [17].

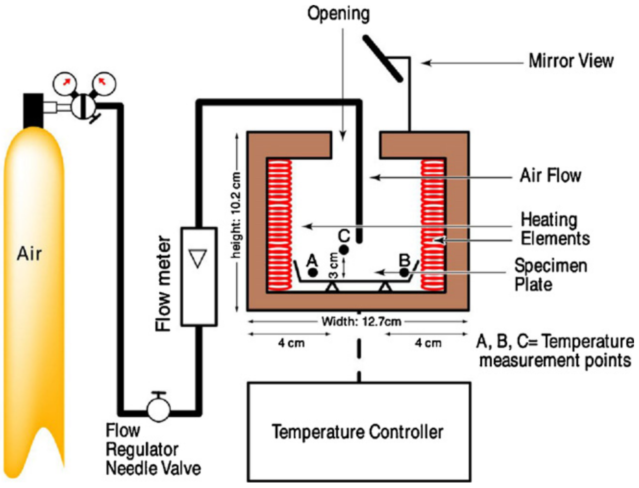


Fig. 1. Diagrammatic presentation of the furnace for measuring self-ignition.

For the experiments of pure $NaHCO_3$, aluminum pan of 40 μl volume capacity was used. The samples were heated using dynamic linear heating ramp rate of 10 °C/min, in 50 ml/min nitrogen (N_2) flow, from 25 °C to 400 °C. TGA and DTA curves have been obtained, in order to investigate the exothermic and endothermic reactions of sodium hydrogen carbonate.

2.1.2. Self-ignition measurements furnace

For self-ignition measurements a specially modified furnace has been used. The internal dimensions of the furnace (Thermolyne model 47900) were 12.7 cm × 10.2 cm × 15.2 cm (width, height, depth). The temperature control accuracy was ±3 °C at 1000 °C. An air flow supply of $1.5\,l\,min^{-1}$ of air (21% O_2, 79% N_2) has been piped from the top of the furnace, providing and assuring an oxidative atmosphere. Oxygen is the necessary component to enable smoldering and ignition, both affecting the charring rate [18].

Three thermocouples A, B, and C were placed into the oven in order to measure the oven temperature, assuring accuracy better than 0.3 °C. The apparatus (Fig. 1) has been fully described in another publication [19].

Time to ignition has been considered as the time from the moment the inserted pellet touched the porcelain pan – sited at the bottom of the furnace – to the moment that the flame appeared (visual detection). The duration of combustion has been considered as the time from the appearance of the flame until extinction. Prior to each test, a period of 20 min was allowed from the previous run, in order to stabilize temperature of the furnace and ensure identical oxidative conditions. All samples were duplicated and the mean values on each case have been used for producing the graphs.

2.2. Materials

The forest species that have been tested as forest fuels, under the affect of $NaHCO_3$ were: *Pinus brutia*, *Laurus nobilis* and *Nerium oleander*. The selection was based on their frequent appearance in the Mediterranean flora. Pyrolysis and combustion samples were prepared from the same primary mass for each of the forest specie. The $NaHCO_3$ used as fire retardant was provided from Sigma–Aldrich Chemie Gmbh.

Table 1
Samples preparation protocol.

Forest species	$NaHCO_3$		
Pinus brutia, *Laurus nobilis*, *Nerium oleander*	20% (w/v) $NaHCO_3$ aqua solution	Supplementary added water	$NaHCO_3$ concentration in the sample
Mass (mg)	Volume (ml)	Volume (ml)	w/w (%)
0.95	25	75	5
0.90	50	50	10
0.85	75	25	15
0.80	100	–	20

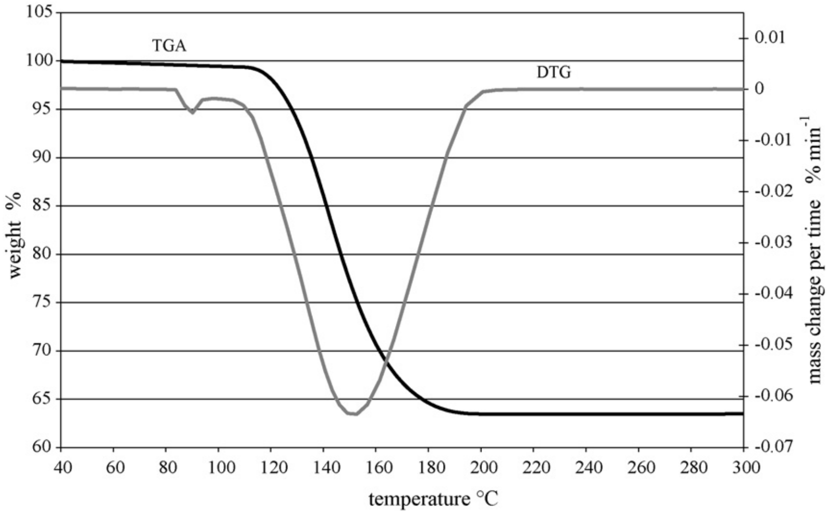


Fig. 2. TGA and DTG of $NaHCO_3$ in nitrogen (N_2).

2.2.1. Sample treatment

Upon sample selection from outdoors, the brushes were dried at 60 °C in a furnace under a vacuum pressure of 100 mmHg, until relatively constant weight of 1 mg was reached. The procedure took was about 48 h. Afterwards, only the pine needles or the leaves from the brushes of the forest species were carefully collected and subsequently they were ground into a seed mill. Grain sizes between 0.3 mm and 0.5 mm were chosen. Four different w/w % of 5%, 10%, 15% and 20% of $NaHCO_3$ were tested on each forest specie. In order to achieve homogeneous samples, the sodium bicarbonate has been added as an aqua solution of 20 w/v. Extra water was added to make up a volume of 100 ml in order to attain uniform dispersion of $NaHCO_3$.

The procedure employed in this study is summarized in Table 1.

After stirring, the samples were left to dry at 60 °C for 48 h under a vacuum pressure of 100 mmHg.

a. Pyrolysis experiments (TGA): the samples for pyrolysis came from the mass of the treated forest specie mass (describe above), as dry powder.
b. Self-ignition experiments (tested at the furnace; Fig. 1): for self-ignition measurements, mass of 1 g treated powder (Table 1) was

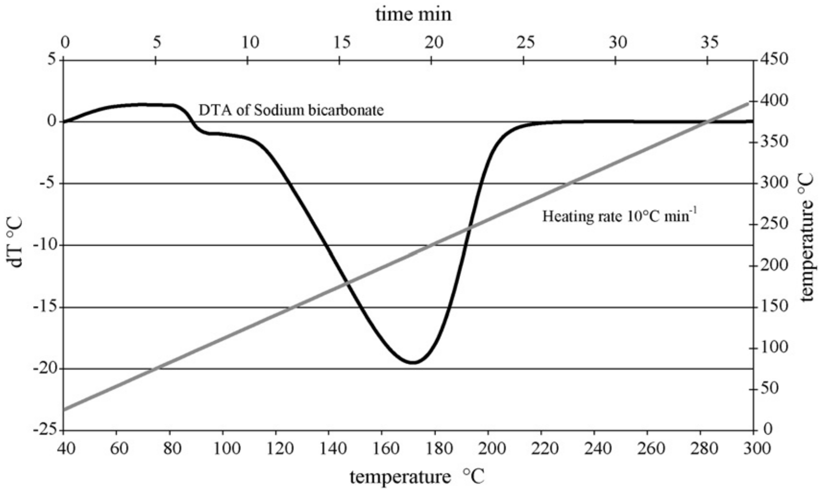


Fig. 3. DTA of $NaHCO_3$.

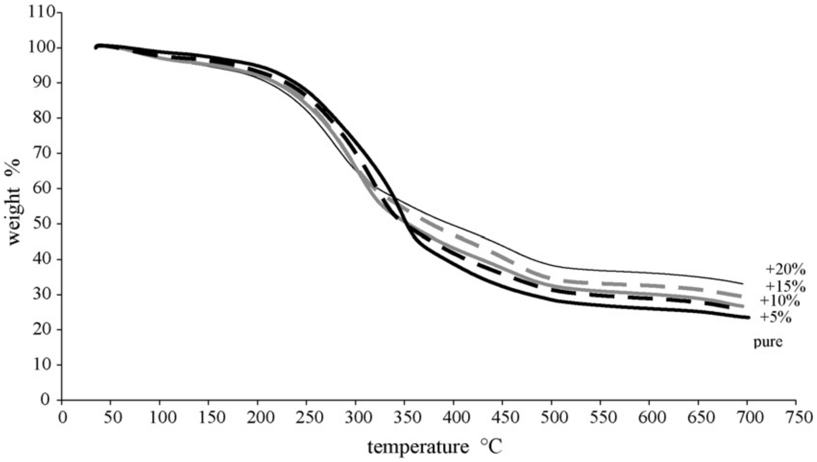


Fig. 4. The effect of $NaHCO_3$ on *Pinus brutia* (TGA).

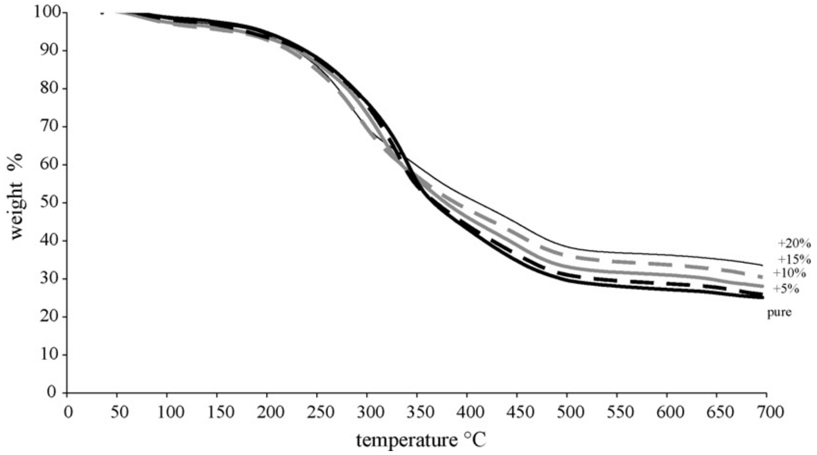


Fig. 5. The effect of $NaHCO_3$ on *Laurus nobilis* (TGA).

pressed under a pressure of 155 atm (15.7 MPa) in order to form cylindrical and well compact mass pellet of 1.3 cm diameter. The height of each pellet was approximately 6 mm (±1 mm). Height variation was due to the bulk density of forest specie.

As humidity is very important and it is influencing the duration of carbonization [20] all the samples were stored in a desiccator to maintain the same humidity until ignition test.

3. Results and discussion

3.1. Thermal degradation of $NaHCO_3$

In order to investigate the effect of $NaHCO_3$ on the mass residue and interpret the TGA results, the thermal degradation of $NaHCO_3$ have been studied (Fig. 2).

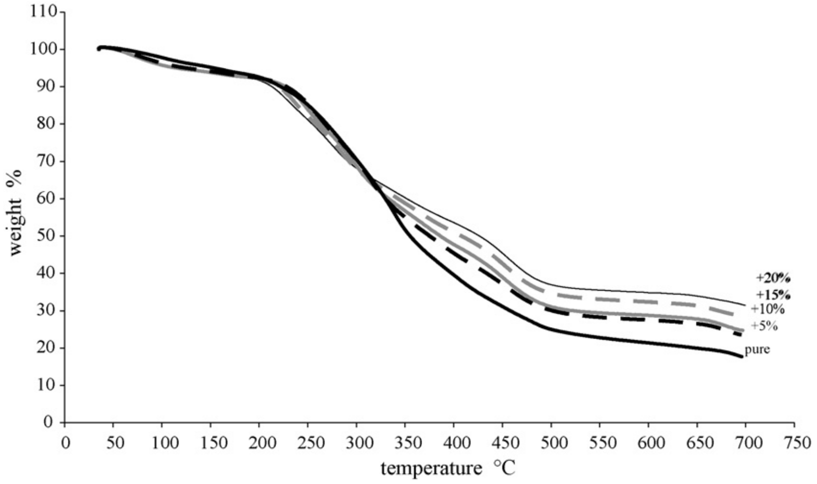


Fig. 6. The effect of $NaHCO_3$ on *Nerium oleander* (TGA).

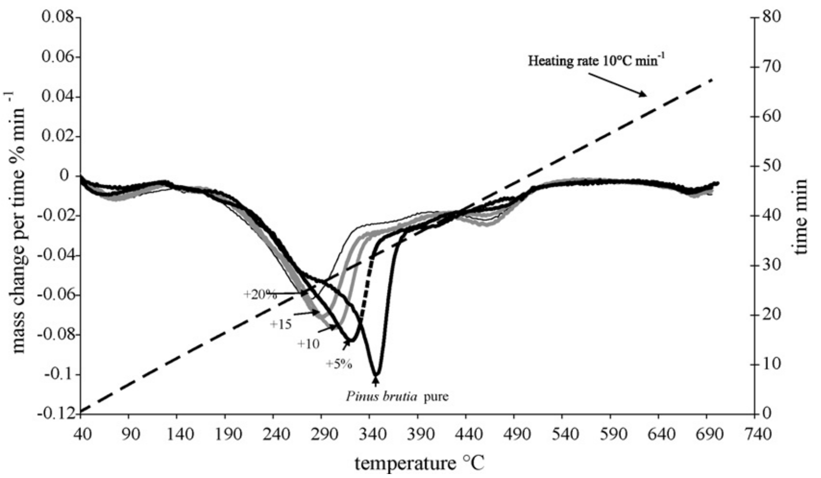


Fig. 7. The effect of $NaHCO_3$ on *P. brutia* (DTG).

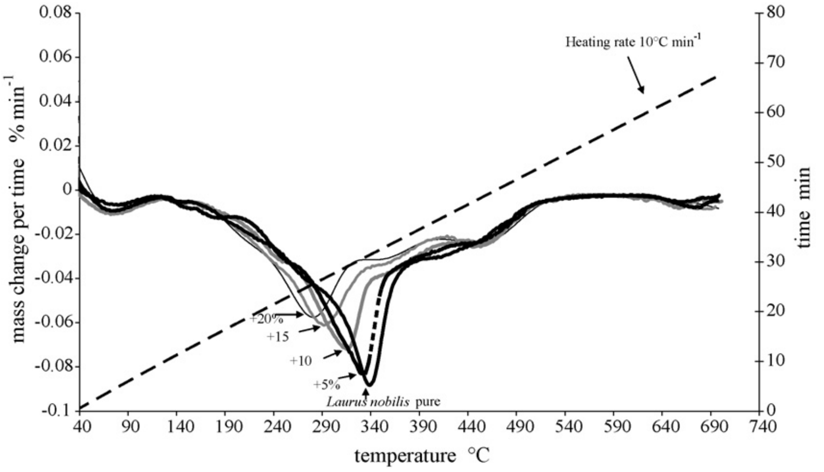


Fig. 8. The effect of $NaHCO_3$ on *L. nobilis* (DTG).

The weight is constant up to a temperature of 120 °C and then drops rapidly until a temperature of about 190 °C is reached and the levels off.

Using the TGA curves of the pure $NaHCO_3$ (Fig. 2) and the TGA curves of the pure forest specie (Figs. 4–6) new TGA curves have been calculated for $NaHCO_3$ concentration 15% (w/w). Comparisons of the new curves have been made with the TGA results of the tested samples (Table 1), in order to investigate if the effect of $NaHCO_3$ on mass residue is additive or synergistic (Fig. 10a–c).

It is clearly evident from $NaHCO_3$ DTA (Fig. 3) that the thermal degradation of $NaHCO_3$ requires energy in order to decompose

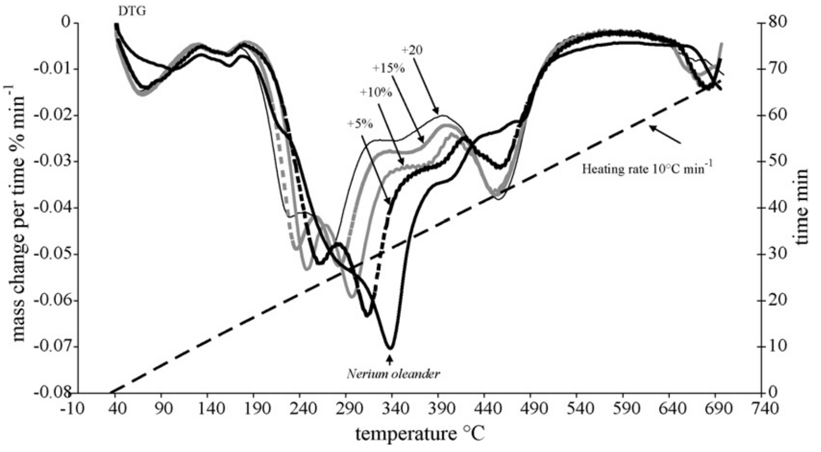


Fig. 9. The effect of $NaHCO_3$ on *N. oleander* (DTG).

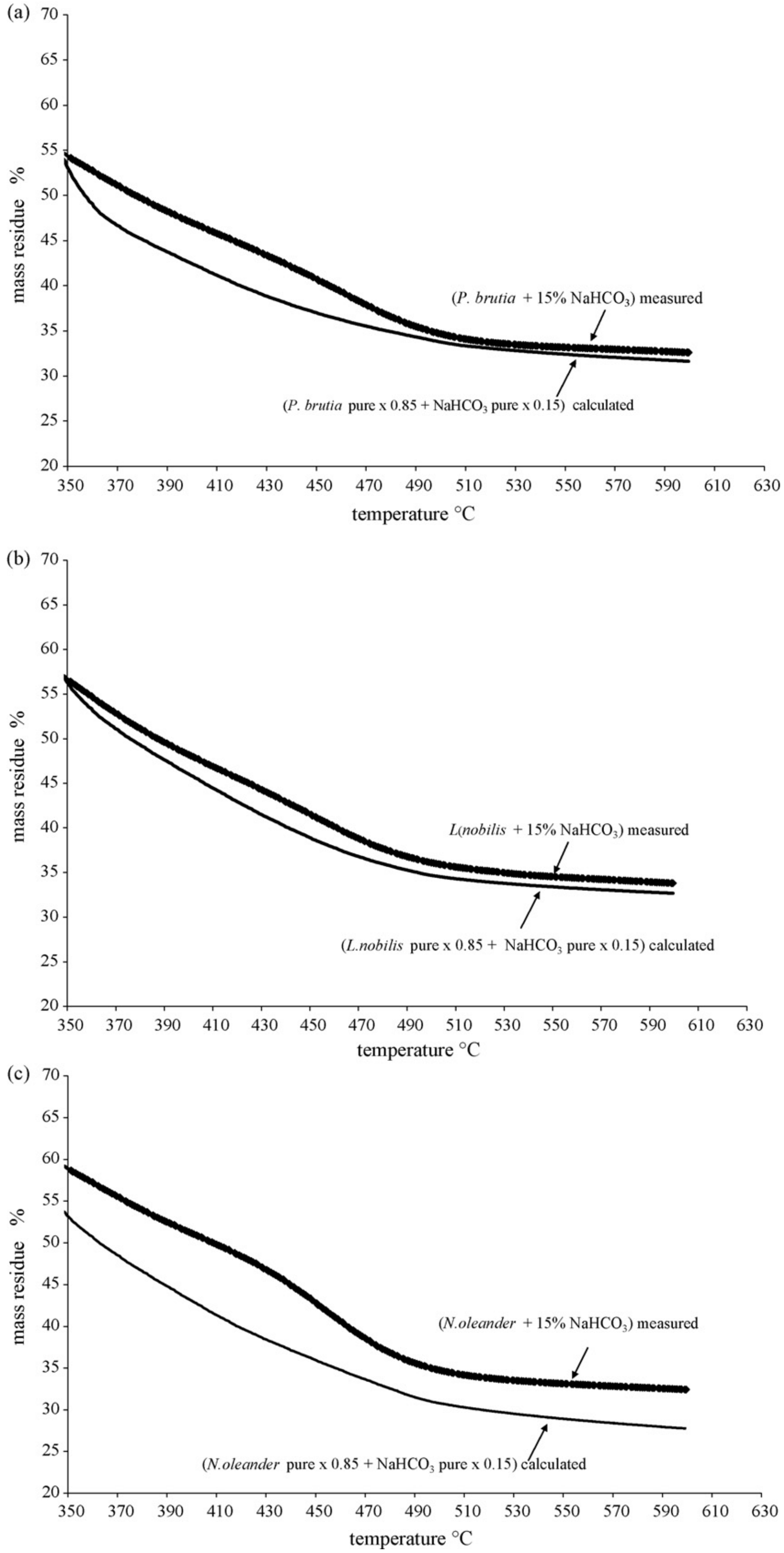


Fig. 10. The effect of $NaHCO_3$ on (a) *P. brutia*, (b) *L. nobilis* and (c) *N. oleander* on the mass residue showing calculated and measured values.

and form Na_2CO_2(s), CO_2(g) and H_2O(l). Hence, sodium bicarbonate acts as fire retardant in three ways. Firstly, it drains energy in order to decompose the material, secondly it emits CO_2(g), which is commonly used to put out fires because it deprives the ignition process of oxygen required for combustion and thirdly it emits H_2O(l) which converts from liquid to vapor consuming energy, that would otherwise be used to initiate ignition.

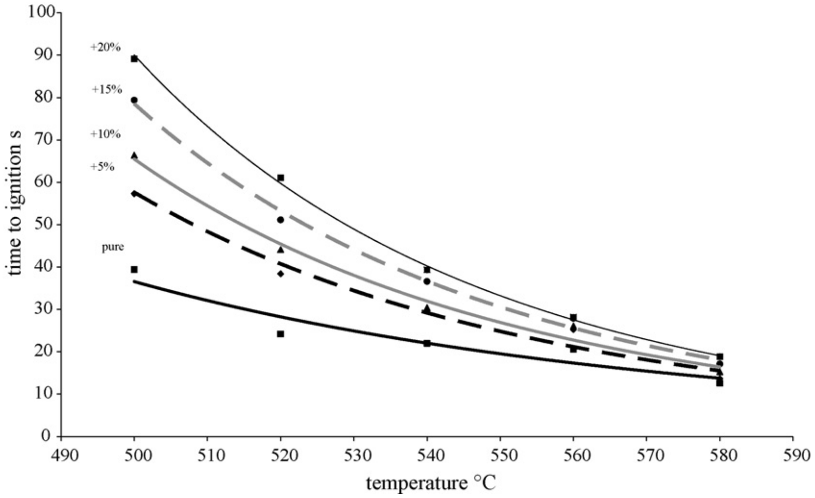


Fig. 11. Time to ignition of *P. brutia* treated with different concentrations of $NaHCO_3$.

3.2. Pyrolysis of forest species with $NaHCO_3$

3.2.1. TGA P. brutia, L. nobilis and N. oleander treated with $NaHCO_3$

TGA was used to investigate the effects of sodium bicarbonate on the pyrolysis of the various forest species. Figs. 4–6 demonstrate that the $NaHCO_3$ seems to increase the relative formation of char residue of *P. brutia*, *L. nobilis* and *N. oleander*. As discussed later this increase has proved to be misleading for *P. brutia* and *L. nobilis* and it was not due to the effect of $NaHCO_3$ but because of the decrease from 100% to 80% in the mass of the forest specie contained by the sample thus having an additive effect.

To the only forest specie in which $NaHCO_3$ seemed to have a synergistic instead of additive effect was *N. oleander*. In particular, *N. oleander* was the only one among the three forest specie in which the main thermal degradation comprises of two steps rather than one.

3.2.2. (DTG) Thermal degradation of P. brutia, L. nobilis, N. oleander treated with $NaHCO_3$

In order to examine the thermal degradation steps of the forest species, DTG curves were used. Figs. 7 and 8 show that $NaHCO_3$ induces a shift towards lower thermal degradation temperatures for *P. brutia* and *L. nobilis*. The maximum shift occurred for the samples containing 20% (w/w) $NaHCO_3$ in both cases and it was approximately 70 °C lower compared to the pure *P. brutia* and 65 °C lower compared to the pure *L. nobilis*.

The DTG curves reveal several peaks for each of the three considered forest species. It is highly likely that the peaks are related to kinetic steps during the thermal degradation process. Detailed studies are required to attribute the peaks to individual steps in the decomposition process. However, it is evident that as $NaHCO_3$ is added, in all cases investigated, there are two effects. Firstly, there is a shift in all of the peaks toward a lower temperature and secondly the peaks become less pronounced; both supported the premise that the $NaHCO_3$ is an effective fire retardant. The difference in the curves is more pronounced with *N. oleander* compared to the other two species. This is due to the variation in the composition of the species in terms of the presence of hemicellulose, cellulose and lignin. *N. oleander* is the only among the three forest species which shows two major steps (peaks) between 200 °C and 360 °C (Fig. 9). Notably, the first peak may be attributed to the increased contain of hemicelluloses compared with *P. brutia* and *N. oleander*.

3.2.3. Effect of $NaHCO_3$ on the mass residue

As has already mentioned (Section 3.1), the effects of the $NaHCO_3$ on the mass residue were also investigated using calculated TGA curves in comparison with curves obtained from TGA runs.

The results are depicted in Fig. 10a–c.

In general the mass residue decreased along with temperature increase. The trends were similar in all the species investigated. The calculated values were determined by measuring the mass residue individually, firstly of the specie and then of the additive. These values were then added together to formulate the calculated curves, that have been plotted on the graph shown in Fig. 10. A mass residue difference (0.96% and 1.12% at 600 °C, respectively) occurred between the measured and the calculated values for *P. brutia* and *L. nobilis*, evoking an additive effect.

However for *N. oleander* measured and calculated curves showed a bigger mass residue difference of 4.68% at 600 °C (Fig. 10c). This may be due to a synergistic effect, where the combined effect of the additive and the pure specie were greater than the sum of the two, measured individually. This may be due to additional interaction between the additive and the natural ingredients of the specie and particular of the hemicelluloses (Fig. 9). This merits further investigation in order to obtain a better understanding of these phenomena.

3.3. Combustion

3.3.1. Time for self ignition

The times to self ignition were measured as discussed in Section 2.1.2 and the results for the three different forest specie treated with $NaHCO_3$ are presented in Figs. 11–13.

It is evident from the figures mentioned above, that as the temperature increased reaching 580 °C, the difference in ignition times of the samples treated with different content of sodium bicarbonate became less pronounced. An explanation of this behavior follows:

Firstly, the delay in ignition times at a given furnace temperature is due to the early decomposition of $NaHCO_3$ (as evidenced from the TGA results at Fig. 2) into CO_2 and H_2O which both contribute to the delay of ignition. This delay increases with higher levels of $NaHCO_3$ for a given temperature in the furnace as more CO_2 and H_2O are released. Thus, the composition of the emitted gases, issuing from the pyrolysis of the fuel is becoming less flammable.

The delay of self ignition can be also explained as the result of the increase of an effective ignition temperature or a critical heat flux

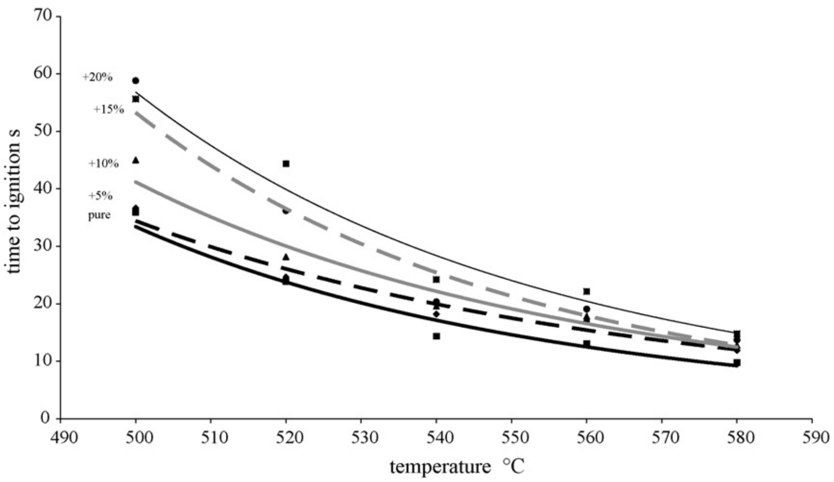


Fig. 12. Time to ignition of *L. nobilis* treated with different concentrations of $NaHCO_3$.

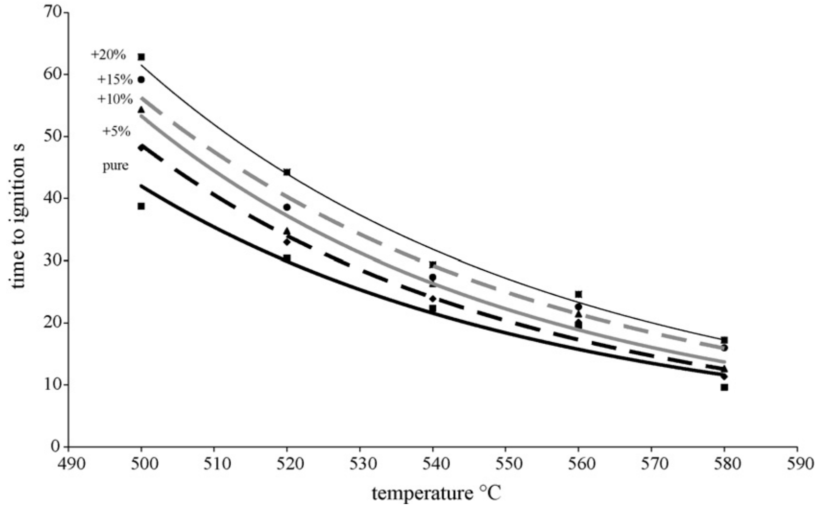
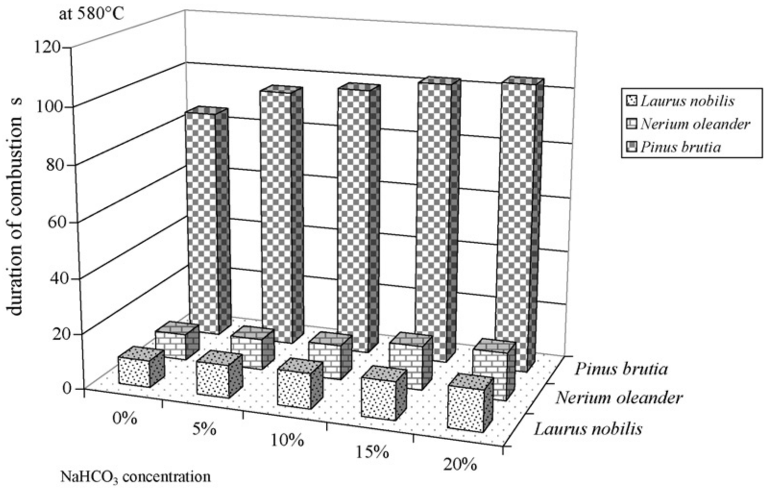


Fig. 13. Time to ignition of *N. oleander* treated with different concentrations of $NaHCO_3$.



	0%	5%	10%	15%	20%
▨ Laurus nobilis	9.77	11.89	12.77	13.74	14.78
▤ Nerium oleander	9.61	11.33	12.64	15.99	17.24
▩ Pinus brutia	85.4	95.38	98.25	102.41	104.36

Fig. 14. Duration of combustion of *P. brutia* treated with different concentrations of $NaHCO_3$ at 580 °C.

as the mass concentration of $NaHCO_3$ increases [21]. It is difficult to completely quantify the ignition process in this experiment because the heat flux imposed to the sample is not well defined. This heat flux consists of radiative, convective and conductive (to the base of the furnace see Fig. 1) components. The time to ignition will increase as the net heat flux, i.e. the difference between the imposed heat flux and the critical heat flux decreases.

Secondly, following, the previous observations, we note that the relative decrease in the time to self ignition as the temperature increases (see Figs. 11–13) can be explained by noting that the relative magnitude of the net heat flux decreases as the temperature (and hence the imposed heat flux) increases.

In this paper, only time to self ignition have been recorded; which is totally different from the time to piloted ignition. Piloted ignition occurs in less time than the time to self ignition and at much lower fuel temperatures (300 °C instead of 500–600 °C) and so it could be influenced by the fire retardant in a different way.

3.3.2. Duration of combustion

The duration of combustion increased with the addition of $NaHCO_3$ as Fig. 14 and the associated table show for a furnace temperature of 580 °C. That means also that the heat released rate decreased if we assume that the total heat released remains the same for all fire retardant concentrations. Similar results were obtained for the other furnace temperatures tested in this study.

However, the difference in the time of combustion for the specie considered is pronounced. The increase of the burning time of the volatiles is attributed to a heat of pyrolysis of *P. brutia* higher than the heat of pyrolysis of the other two species. This higher heat of pyrolysis decreases the mass burning rate (and so increases the burning time) because the imposed heat flux is the same at a given temperature of the furnace. The differences observed in the various forest specie studied are due to the composition of the specie regarding the amount of hemicellulose, cellulose and lignin.

4. Conclusions

For all three forest species, the thermal degradation profile was shifted towards lower temperatures. This means that $NaHCO_3$ induced an early emission of the volatile gases by influencing the kinetics of hemicelluloses and cellulose.

As far it concerns the effect of $NaHCO_3$ on the mass residue, on *P. brutia*, *L. nobilis* was additive and synergistic to *N. oleander* as explained.

Time to ignition increased by adding $NaHCO_3$. That was due of the alteration of the composition of the emitted flammable gases at the vicinity of the sample, due to the release of water (H_2O) and carbon dioxide (CO_2) produced by the decomposition of sodium bicarbonate. On top, additional energy was needed for the system to reach ignition conditions due to the thermal decomposition of the sodium bicarbonate.

The duration of combustion increased slightly with the addition of $NaHCO_3$ as Fig. 14 and the associated table show, for a furnace temperature of 580 °C. Similar results were obtained for the other furnace tested temperatures in this study. The difference in the duration of combustion was, however, significantly greater for *P. brutia* compared to the two other species. Thus, sodium bicarbonate decreases the threshold of initial temperature of pyrolysis of forest species (promotion effect). On the other hand $NaHCO_3$ increases the self ignition delay time and combustion duration of forest species (inhibition effect). In addition the presence of $NaHCO_3$ increases the pyrolysis mass residue of forest species, especially when sodium carbonate applied on *N. oleander*.

Overall, $NaHCO_3$ exhibits a satisfactory fire retardant performance on lignocellulosic materials, in terms of reducing time to self ignition, mass residue and should be considered important long term fire retardant additive for the suppression of wild land fires.

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