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TG AND AUTOIGNITION STUDIES ON FOREST FUELS

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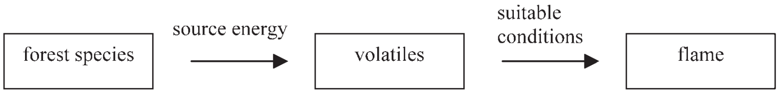
Abstract

The autoignition delay times of some important Mediterranean forest species: *Arbutus adrachne, Abies cephallonica, Pinus brutia, Pinus halepensis, Pistacia lentiscus, Cupressus semprevirens, Olea europaea, Cistus incanus* were determined in the range 460–600°C under precisely controlled temperature and airflow conditions. Based on these data the forest fuels examined were classified into two groups: the least and the most flammable species. The autoignition delay data were related to the thermal analysis measurements. The themogravimetric analysis in an inert (nitrogen) atmosphere showed that the thermal decomposition of cellulose in the range of 300–400°C as well as the mass residue at 600°C are directly related to the ignition behavior.

Keywords: autoignition delay, forest, TG

Introduction

A forest sample exposed to a sufficiently high heat flux in the absence of a pilot source may ignite spontaneously, if the fuel vapors/ air mixture is at a sufficiently high temperature. The general scheme for spontaneous ignition is



If a forest sample is situated in a hot vessel, at certain values of temperature and air flow, a spontaneous ignition is observed after an *ignition delay* time sometimes called *induction time*. Thus, ignition delay is the time between the first con-

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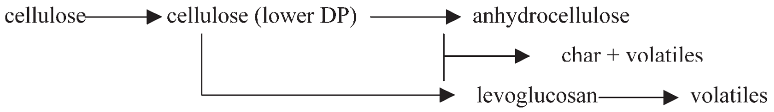
tact of reactants (forest fuel-air) at high temperatures and the formation of visible flame and can be as long as several minutes or as short as fraction of seconds [1].

Spontaneous ignition delay provides a measure of ignitability of materials studied and is usually determined under various heat flux levels using standard methods [1]. The main parameters affecting ignition delay are: temperature, solid fuel particle size, chemical composition of the fuel, oxygen concentration, apparatus characteristics.

During the induction time, dehydration and volatilization of organic substances, i.e. essential oils (mainly terpenoid hydrocarbons), occur. It follows the pyrolysis of the forest fuels. Pyrolysis breaks down the substance molecules into low molecular mass gases (volatiles), tars, carbonaceous char and mineral ash. Among the pyrolysed components primer importance has cellulose, which is a principal component in forest species, comprising 41–53 mass/mass% of the total mass. Cellulose is a linear condensation polymer that consists of *D*-glucose units linked by β-1,4-glucosidic bonds.

The thermal degradation of cellulose, according to a popular theory [2–7], takes place between 250–400°C and follows two competing pathways. One is the dehydration which leads to char and gases (mainly CO, CO_2, H_2O) and the other is the depolymerisation which leads to tar and volatiles through the formation of levoglucosan, as is it shown below:



The rich variety of reaction products evolved when cellulose is heated implies very complex pyrolysis chemistry. Almost one hundred compounds were detected by GC-MS [8]. The products of cellulose pyrolysis include many oxygenated products, such as methanol, glycolaldehyde, levoglucosan and oligomers and also methane.

Hemicelluloses comprise 15–25 mass/mass% of the forest species. They are carbohydrate polysaccharides with shorter chain lengths than cellulose consisted of *D*-xylose, *D*-mannose, *D*-glucose, *D*-galactose, *L*-arabinose, *L*-rhamnose, 4-O-methyl-*D*-glucuronic acid, *D*-glucuronic and *D*-galacturonic acid. Hemicelluloses, exhibit similar thermal degradation behavior to cellulose, due to their chemical structure similarities.

Lignin which comprises 16–33 mass/mass% of the forest species is a complex polymer, consisting of four or more phenylpropane monomers per molecule. Its chemical properties as well as physical properties vary not only with the species of wood but also with the isolation method. It is pyrolysed in the temperature range of 280–500°C, contributing more to the char formation [2, 3].

Flammability data such as ignition delay times of forest species are very useful to fire management planning as well as for forest fire retardation studies [9]. Thermal analysis techniques can be used for interpreting the flammability characteristics by measuring the rate and amount of volatilization of forest fuels as a function of temperature [10]. Rogers *et al*. [11] related the TG thermal behavior of a forest material with its chemical composition. Also, Kaloustian *et al*. [12] using DTA and TG correlated the maximum thermal decomposition rate of various Mediterranean plants with their content in cellulose. Cordero *et al*. [13] used TG to study the kinetics of thermal decomposition of *Eucalyptus sawdust*. Other researchers have examined the effects of various fire retardants on the pyrolysis of forest fuels using TG and DTA [14–15]. However, the small samples used in the analytical methods and the rapid removal of pyrolysis and combustion products can lead to an erroneous interpretation in terms of forest fuel ignitability performance in field conditions. Therefore, the information provided by analytical methods should be supported by other tests.

The object of this study is to find the relative flammability of eight Mediterranean forest fuels using autoignition delay time measurements, under precisely controlled temperature and airflow conditions, and to correlate these data with TG analysis data.

Experimental

Apparatus for autoignition measurements

The autoignition tests were performed in a house made apparatus described in details in previous work [16]. It consisted of a furnace with internal dimensions 12.7×10.2×15.2 cm temperature controlled within 1°C. The samples, in the form of cylindrical pellets of 1 g, were dropped into a porcelain plate of 8 cm diameter, located at the bottom of the oven chamber, through a circular opening from the top of the furnace. The oven opening was also used to observe via a mirror any changes in the specimens (ignition, smoking, smoldering, no change) as well as for ventilating the system (removal of combustion gases). A controlled air flow of 1.5 L min^{-1}±10% was admitted at the bottom of the oven through a stainless steel tube, measured by a rotameter. Measurements of ignition delay were conducted at constant airflow and temperature conditions by timing the period from insertion of the sample into the oven until the appearance of the first flame of the fuel.

Thermogravimetry (*TG*)

TG measurements were conducted using the Mettler TG/SDTA 851 module. The analyses were carried out on 10 to 11 mg samples using open type alumina sample holders. The samples were heated from 25–700°C with a linear heating rate of 10°C min^{-1}. All runs were conducted in nitrogen atmosphere at a flow rate of 50 mL min^{-1}, in order to avoid combustion and isolate the pyrolysis step of samples examined.

Samples

Tests were conducted on eight forest fuels: *Arbutus adrachne, Abies cephallonica, Pinus brutia, Pinus halepensis, Pistacia lentiscus, Cupressus semprevirens, Olea* *europaea, Cistus incanus.* The selected forest species are very common in the Mediterranean region and are often devastated by forest fires. Some characteristics of the forest materials tested are shown in Table 1.

Table 1 Forest samples tested

Species	Apparent density/ g mL^{-1}	Heat of combustion/ kJ kg^{-1}	Collection data
Pinus halepensis	0.45	22.185	The sample collection site of *Pinus hal.*, *Pistacia lent.*, *Cupressus sempr.*, *Olea eur.*, *Cistus inc.*, *Pinus brut* was the mountainside Kalopoula of Imitos, near Athens, located W-NW with geographic coordinates 37°58′ N and 23°48′20′′ E, height 487 m and average slope 70%. The dates of collection were 15 March, 7 May and 7 November 2000. The sample collection site of *Arbutus adr.*, *Abie*s *cephal.*, was Ntracisa of the mountain Parnitha, near Athens, located –NW with geographic coordinates 38°10′24′′ N and 23°40′29′′ E, height 900 m and average slope 15%. The date of collection was 12 January 2001. All samples was collected after a long drought period in order to avoid moisture effects
Pinus brutia	0.54	21.380	
Pistacia lentiscus	0.51	22.018	
Cupressus semp.	0.37	19.548	
Olea europaea	0.42	21.373	
Arbutus adrach.	0.53	20.185	
Abies cephal.	0.51	20.695	
Cistus incanus	0.42	21.683	

The heat of combustion of the forest samples was determined by a Parr Instruments Company plain jacket bomb calorimeter, model 1341. The absolute density of the samples after compression in the form of pellets was 1.2 g mL^{-1}.

Sample preparation for the ignition measurements

For each species, a bulk sample comprised of leaves detached from 3–5 individual trees was collected, in order to minimize interspecies differences. After field sampling, the forest species were placed in sealed plastic bags and brought to laboratory. Their preparation was according to the following procedure: The samples were dried at 60^{o}C, under vacuum of 100 mmHg until constant mass within 1 mg. The approximate time of drying 100 g sample was 48 h. The dried sample was then ground and a fraction between 0.3 and 0.5 mm was separated and used for the tests. For the ignition measurements about 1 g of the powder was pressed into a cylindrical pellet of diameter of 1.3 cm at a pressure of 15.7 MPa (155 atm) in order to achieve uniformity in terms of surface to volume ratio and fuel density. The pellets were kept in a desiccator until the time for ignition test.

Procedure

The furnace was set at certain temperature and allowed to reach equilibrium for at least 15 min. In the mean time the flow of the air current through the heating coils was adjusted to 1.5 L min^{-1}. The forest fuel samples were dropped to the furnace vessel through the circular opening from the top of the furnace and the time from insertion of the sample into the oven until the appearance of flame was recorded. In case no flames occurred within 3 min, the test was terminated and the result was recorded as 'non-ignition'.

Results and discussion

The ignition delay time of the forest species tested, in the temperature range of 500–600°C and airflow of 1.5 L min^{-1}, is presented in Table 2.

The measurements reported in Table 2 are the average of five replicate tests, while the relative standard deviations determined were below 10%. From the data shown in Table 2, the curves of ignition delay *vs*. temperature were plotted. These curves show a general trend for higher ignition delay times as the furnace temperature decreases. In the low temperature range where all forest species burn (i.e. 520–540°C), the curves follow the flammability of the fuels, with the least flammable ones leading to higher delay times, Fig. 1. Based on this graph the forest fuels examined were classified into two groups:

1. The least flammable species group: *Arbutus adrachne, Pistacia lentiscus* and *Cistus incanus*.

2. The most flammable species group: *Pinus halepensis, Olea europae, Abies cephallonica, Cupressus semprevirens and Pinus brutia*.

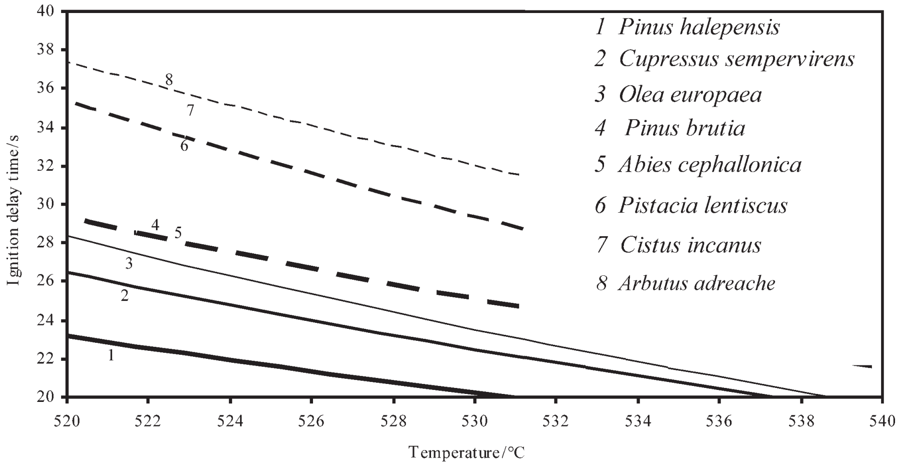


Fig. 1 Autoignitability behavior of forest species, using 1.0 g samples and airflow 1.5 L min^{-1}

Table 2 Ignition delay time/s of forest fuels at various temperatures, using samples of 1.0 g and air flow 1.5 L min^{-1}

Forest species	Temperature/°C														
	460	470	480	490	500	510	520	530	540	550	560	570	580	590	600
Pinus halep.	NI	NI	45	35	30	30	24	21	14	14	14	12	10	10	9.5
Pinus brutia	NI	NI	NI	50	39	33	31	25	21	18	17	14	13	10	9.5
Pistacia lentiscus	NI	NI	NI	NI	NI	NI	33	35	23	18	18	17	12	9.0	9.0
Cupressus sem.	NI	NI	55	43	36	36	27	24	18	12	15	13	11	10	7.5
Olea europ.	NI	NI	57	56	42	35	27	23	22	17	15	10	7.5	9.0	7.0
Cistus incanus	NI	NI	NI	61	48	43	37	31	29	27	21	20	17	12	11
Arbutus adrach.	NI	NI	NI	NI	43	32	29	22	21	18	16	15	11	9	9
Abies cephall.	NI	NI	NI	53	47	31	26	27	20	15	13	13	12	9	7
Arbutus unedo	NI	NI	NI	NI	45	28	29	23	22	20	16	13	12	10	9

NI=no ignition

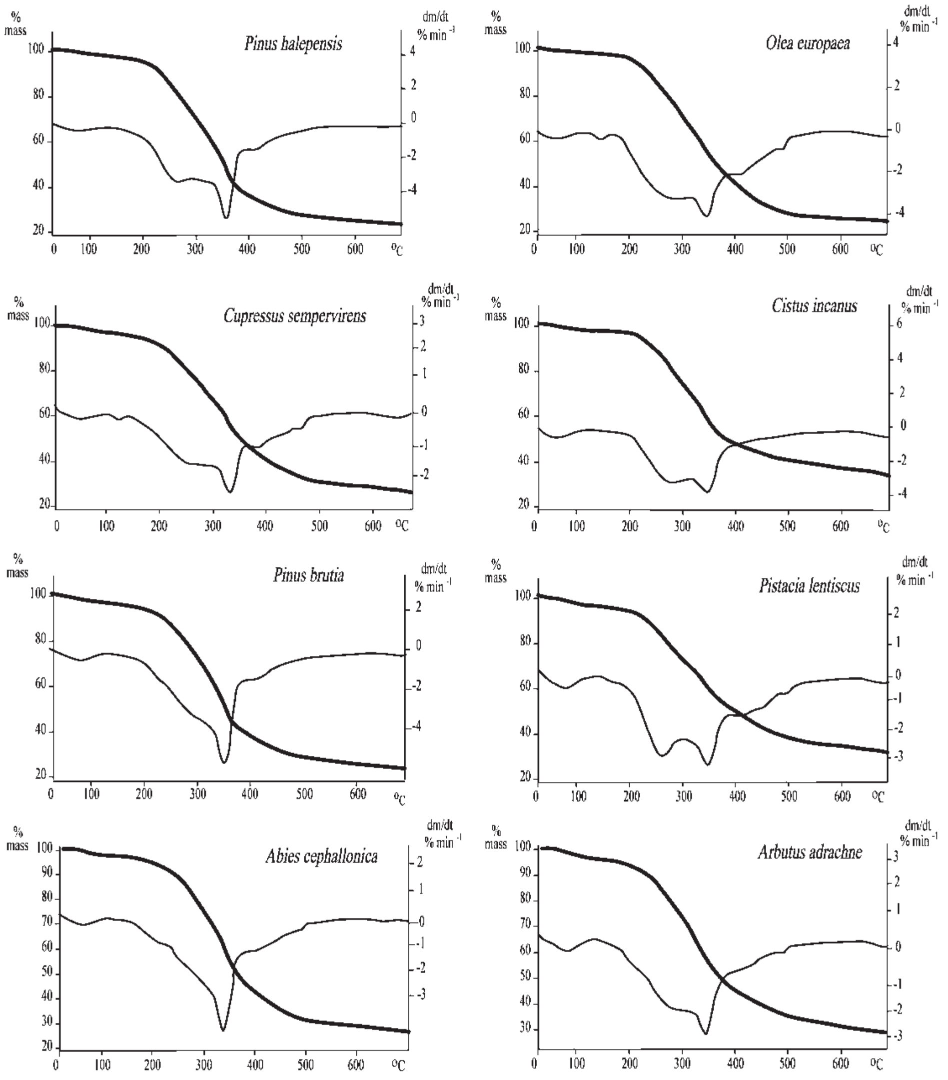


Fig. 2 TG and DTG curves of forest species

TG and DTG curves of the forest species examined in a nitrogen atmosphere are presented in Fig. 2. It is observed that appreciable mass losses take place in five different temperature ranges. The first, in the range of 30–100°C, corresponds mainly to the drying process due to the evaporation of moisture. The second, in the range of 120–160°C, appeared clearly in DTG diagrams of *Olea europaea* and *Cupressus semprevirens*, and is attributed to the evaporation of volatile constituents. The mass loss in the range of 200–280°C corresponds mainly to the hemicelluloses decomposi-

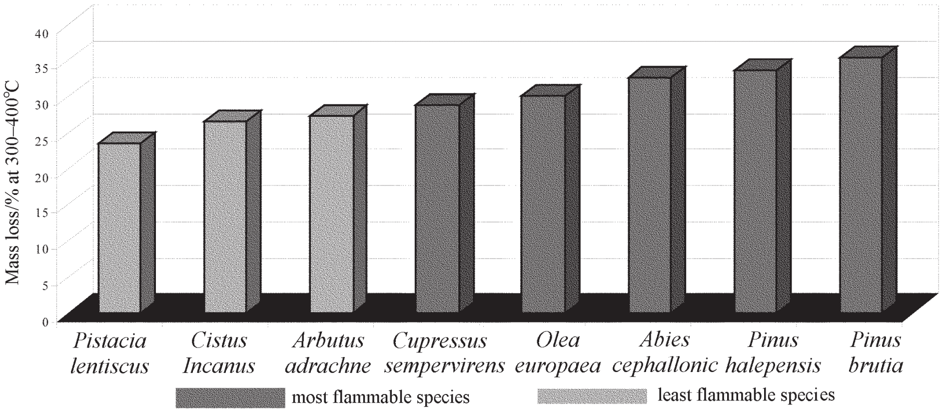


Fig. 3 Mass loss of forest species during pyrolysis in the range of 300–400°C

tion, while the next one between 300–400°C is related to the cellulose decomposition. The last peaks in the range above 500°C are related to the lignin decomposition. It should be noted that the major peak of lignin decomposition usually coincides with the DTG peak of cellulose decomposition. However, lignin decomposition occurs in a wide temperature range and the shoulder above 40°C on the DTG curve can be attributed to lignin decomposition.

All DTG graphs have similar profiles with the major peaks taking place at about 350°C. In all cases the maximum mass loss occurs in the range of 300–400°C, which corresponds mainly to the cellulose decomposition. These major mass losses, presented diagrammatically in Fig. 3, are directly related to the ignitability characteristics of forest species, with the most flammable species having the higher thermal decomposition mass losses (Fig. 4).

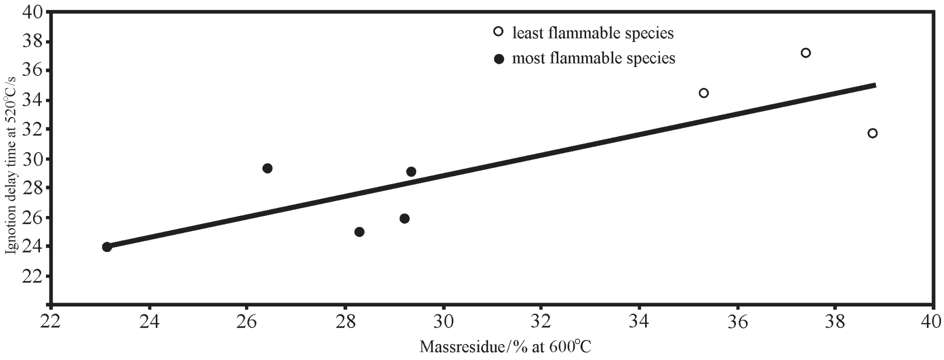


Fig. 4 The relationship between flammability of forest species and mass losses during thermal decomposition of cellulose in the range of 300–400°C

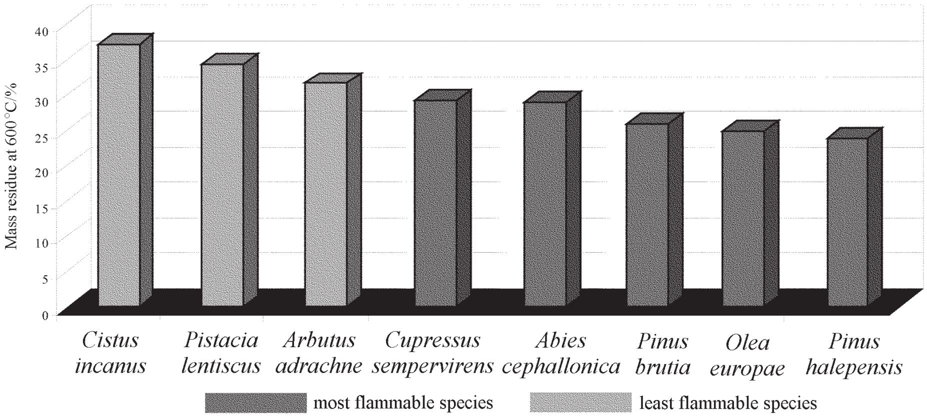


Fig. 5 Mass residues of forest species at 600°C

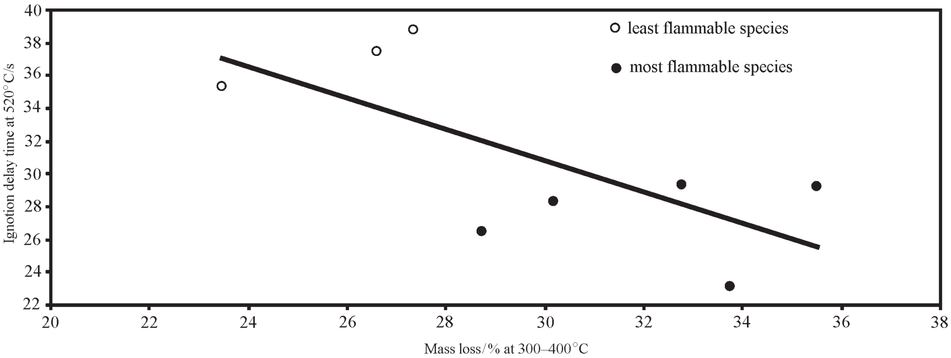


Fig. 6 The relationship between flammability of forest species and mass residues after pyrolysis at 600°C

Based on the TG data, the mass residues at 600°C were determined, Fig. 5. The mass residues were also related to the ignition properties, since the least flammable fuels leave higher mass residues (Fig. 6). This behavior is expected, since the least flammable fuels contain less volatile matter and higher residues.

Conclusions

The flammability of forest fuels is a complex phenomenon, which cannot be adequately assessed in the field due to the influence of many variable environmental factors that cannot be controlled or monitored. Laboratory autoignition delay time measurements provide a very simple method to monitor the flammability of forest species. The relative flammability data provided by this method are very important to forest fire management, i.e. it facilitates the selection of the appropriate afforestation species for reducing wildfire danger.

The ignition properties of forest species determined at laboratory scale may be interpreted by DTG analysis data. The ignitability depends mainly on the amount of cellulose decomposed during pyrolysis, as well as on the total mass residue after thermal treatment up to 600°C. In conclusion thermal analysis data may facilitate to a better understanding of the mechanism of ignitability.

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