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KINETIC STUDY OF THE THERMAL DECOMPOSITIONS OF BIOPOLYMERS EXTRACTED FROM VARIOUS PLANTS

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Abstract

A knowledge of the kinetics of decomposition of biopolymers on heating is important mainly in two domains: forest fires and the incineration of biomass for the production of electric energy. For the study by thermogravimetry of biopolymers (cellulose, holocellulose and lignin), samples of several Mediterranean plants were used.

The cellulose decomposition fits well with apparent first-order kinetics. The activation energy in an air flow is about 185 kJ mol^{-1}. It ranges between 149 and 200 kJ mol^{-1} for holocellulose (cellulose+hemicellulose) in an air flow. Under nitrogen, the values are higher. Differences in the chemical structures of the hemicelluloses (pentosan and hexosan) may explain these variations. The lignins also display various chemical structures. We observed large differences in the thermal decompositions of the various samples. The decomposition rate is increased in a nitrogen flow containing 6% oxygen. We observed a correlation between the maximum decomposition rate and the heating rate. This variation presents a particular form (linear with two slopes). Only the second part seems to be interesting.

Keywords: cellulose, DTG, holocellulose, lignin, thermal decomposition

Introduction

In Provence, the ignition of Mediterranean plants in forest fires involves the volatilization of flammable products: either essential oils (mainly terpenic hydrocarbons) or gases evolved during the decomposition of less volatile components, such as biopolymers.

On the other hand, the search for new, cleaner methods of electric power generation mainly involves use of the biomass-feed flash a pyrolysis process. The engineering design of modern biomass gasifiers and flash-pyrolysis reactors requires a deep knowledge of the biomass pyrolysis kinetics. Since dry biomass fuels typically consist of about 20–50% cellulose by mass, the kinetics of biopolymer pyrolysis is often of primary interest to those responsible for reactor design.

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As the amount of cellulose produced each year is greater than that of all other organic polymers, an understanding of its thermal decomposition is an important goal for the scientific community.

For all these reasons, the kinetics of pyrolysis of cellulose and other biopolymers (holocellulose and lignin) is currently a topic of great interest worldwide. Thermal analysis techniques (TG, DTG, DTA and DSC) can play an important role in the determination of the decomposition kinetics of these biopolymers.

After the collection of the plants, the parts to be studied were dried at 110°C, then ground and sieved. In this way, we obtained homogeneous samples. During heating, these powders always display a first maximum decomposition rate in the DTG curves at about 300–350°C, caused by evolved flammable volatiles, and another at about 400–450°C, corresponding to the combustion of the char [1].

It was demonstrated earlier that the maximum decomposition rate of the plant in powdered form, at about 300°C, is closely connected with the cellulose content [2]. We evaluated the apparent activation energy of this decomposition (about 175 kJ mol^{-1}) by thermal analysis in an air flow. The cellulose content of the plant is almost certainly responsible for the fire during heating. Cellulose turns first into levoglucosan, and then by decomposition to evolved flammable volatiles. Other biopolymers such as holocellulose (a mixture of cellulose and hemicellulose) and lignins can produce flammable products in the same way, even if their decomposition is less important than that of cellulose [2, 3].

In an earlier study, on Aleppo pine (*Pinus halepensis*), the activation energy of the decomposition (first-order kinetics) of the dried powder of the brown cones (open and without seeds) was 179.2 kJ mol^{-1}. For cellulose and holocellulose from the same sample of cones, the activation energy was 181.2 and 160.7 kJ mol^{-1}, respectively. It was not possible to use this kinetic model for the decomposition of the lignin [4].

We have continued these studies with some Mediterranean plants able to burn in forest fires, and also suitable for use as biomass feed in pyrolysis reactors. We present here results obtained on the heating of biopolymers, with the use of thermal analysis, under various gas flow conditions.

Experimental

Samples

The following plants used in this study were collected in Marseille and the surrounding area: *Ulex parviflorus, Quercus coccifera, Acacia dealbata, Pinus halepensis, Rosmarinus officinalis* and *Thymus vulgaris.*

The collection dates are characterized by six digits: day, day, month, month, year, year. Some hours after the picking, the leaves (or needles), branches, flowers and/or fruits were separated.

First, we determined the essential oil content on a part of the freshly picked plants, according to the French Pharmacopoeia. A second portion was dried at 110°C for 15 h, with determination of the mass loss. The samples were then ground and sieved. The powder was passed through a 1 mm sieve. These powders were investigated for the contents of:

– mineral ash obtained after 1 h at 650°C;

– cellulose (by gravimetry), after reaction with a 1:4 *v/v* mixture of concentrated nitric acid and ethyl alcohol [5];

– extractives, by reaction with a 2:1 *v/v* mixture of benzene and ethyl alcohol, with a Soxhlet apparatus [6].

From the residue remaining after the Soxhlet extraction, we determined the lignin and the holocellulose contents. The lignin was determined by gravimetry after 24 N sulfuric acid attack [6]. The holocellulose (i.e. cellulose and hemicellulose) was also determined by gravimetry, after the reaction of the powder with sodium chlorite in acetate buffer at pH 4.9 [5].

All the results are presented relative to the dry matter content (%DM).

Thermal analysis

The biopolymers (cellulose, holocellulose and lignin) obtained by this procedure were tested by simultaneous thermal analysis. A DTA-TG Setaram 92 apparatus with platinel thermocouples was used, with heating rates between 1 and 70°C min^{-1} from room temperature to about 850°C, under an air flow (a mixture of 22% oxygen+78% nitrogen), or using a mixture of 6% oxygen+94% nitrogen, or under pure nitrogen, at a flow rate of 0.5 l h^{-1} in each case. The sample mass of biopolymers was between 20 and 30 mg, the samples were put in platinum crucibles. The mass of the crucibles was about 350 mg.

The DTG curves (decomposition rate) are presented as mass loss % min^{-1}.

Results and discussion

The mass loss during the thermal analysis of the biopolymers is characterized by 3 stages of degradation:

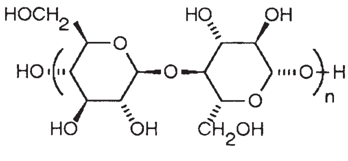
1. up to about 150°C: loss of moisture content in an endothermic reaction;
2. between 150 and about 400°C: decomposition of the biopolymer, with char formation and the evolution of gas (exothermic reaction);
3. between 400 and about 500°C: combustion of the char (exothermic reaction).

The cellulose and hemicellulose components of the whole biomass decompose independently of one another. Lignin decomposition is formally described by a very broad DTG peak at about 300°C [7].

The results obtained for cellulose, holocellulose and lignin are presented separately below.

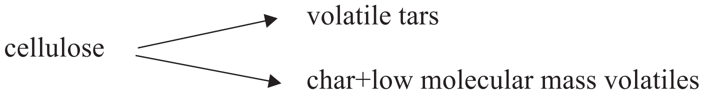
Cellulose

The rich variety of reaction products evolved when cellulose is heated implies very complex pyrolysis chemistry. 96 compounds are evolved and detected by GC/MS [8]. The products of cellulose pyrolysis include many oxygenated products, such as methanol, glycolaldehyde, levoglucosan and oligomers, and also methane.

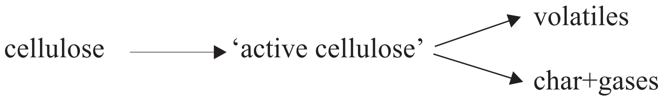


Cellulose

In the mid-1970s, studies on the smouldering and flaming combustion of cellulose led to the mechanism proposed by Broido *et al.* [9, 10], according to the model given below:

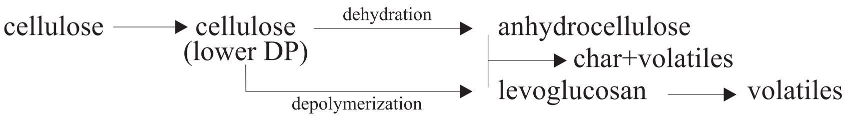


A second model, proposed by Bradbury *et al.* [11], is shown below:

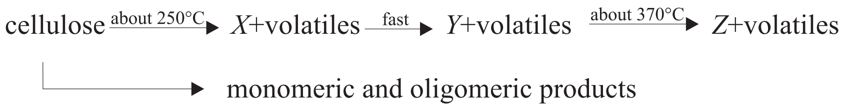


The reaction 'cellulose→active cellulose' is not accompanied by mass loss; hence, there was no direct proof of its occurrence in thermal decomposition experiments. This reaction either occurs before the start of the mass loss, or does not take place at all. Another possibility is simultaneous formation (from cellulose) and decomposition of 'active cellulose' already present [12].

The thermogravimetric study of Whatman filter paper (ash<0.06% mass/mass) and cotton wool under a nitrogen flow supports the scheme given by Alves and Figueiredo [13, 14]:



Extending the study from 250 to 370°C, Várhegyi *et al.* [15] proposed the following reaction scheme:



$$\begin{tikzcd}
\text{cellulose} \arrow[r, "\text{about }250^\circ\text{C}"] \arrow[dr] & X\text{+volatiles} \arrow[r, "\text{fast}"] & Y\text{+volatiles} \arrow[r, "\text{about }370^\circ\text{C}"] & Z\text{+volatiles} \\
 & \text{monomeric and oligomeric products} & &
\end{tikzcd}$$

where X, Y and Z are solid intermediates.

A model of first-order kinetics of the form

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=A\exp\left(-\frac{E}{RT}\right)(1-\alpha)$$

was applied, where α is the fraction of volatiles formed at time t, E is the apparent activation energy, and A is the pre-exponential factor.

Using this model, Cooley and Antal [16] obtained a good fit to the experimental mass loss curves with a value of E of about 193 kJ mol^{-1}.

The complexity of the phenomena, which arise during the heating of cellulose, can seldom be described by a single kinetic equation. However, it has been shown that first-order kinetics fits well with the data obtained, even at elevated pressures, or under an inert gas flow [17–19].

The water content affects the decomposition of cellulose during heating. For example, the heat capacity increases slightly in the case of a 0 to 10% water content, but increases strongly above 10% water. The water content has a protective effect against cellulose decomposition [20]. Therefore, the different cellulose samples were dried at 110°C before testing by thermal analysis.

In thermogravimetry, at a selected value of conversion, the temperature T (in K) at that conversion level is measured for each thermal curve. A plot of the logarithm of the heating rate (β) *vs.* the corresponding reciprocal temperature at constant conversion is prepared. The plotted data should produce a straight line. The activation energy (E) is determined from the slope by the method of Flynn and Wall [21, 22].

$$E=-R\frac{\mathrm{d}\log\beta}{\mathrm{d}(1/T)}$$

where R is the perfect gas constant.

Kissinger [23] presumed that the maximum in the reaction rate practically corresponds to the DSC maximum peak ($T_{\max}$). Ozawa [24, 25] proposed an approximate method for the determination of E from $T_{\max}$. In the Ozawa method, $\log\beta$ is plotted *vs.* $1/T_{\max}$, and the slope of this plot is again $-E/R$ [26].

In an earlier study [27], we observed practically the same values of E via computation by the Flynn method [28], and by using the temperature of the minimum DTG peak.

Using the first-order kinetic model, we evaluated the apparent activation energy (E) during the pyrolysis of cellulose at about 300–350°C.

First, we determined the temperature at the minimum of the DTG curve (T_{min}), which corresponds to the maximum decomposition rate. We then plotted $\log\beta$ *vs*. the reciprocal of the minimum DTG peak temperature (T_{min}), β being the heating rate. For illustration, the results for the thermal degradation of cellulose from the thorns of *Ulex parviflorus* are given in Figs 1 and 2.

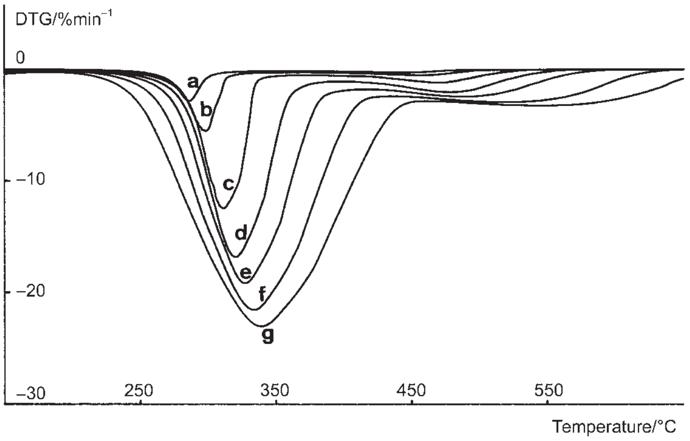


Fig. 1 DTG curves of cellulose extracted from the thorns of *Ulex parviflorus*, in a 22% oxygen flow; heating rate: a=1; b=2; c=5; d=10; e=15; f=22 and g=30°C min^{-1}

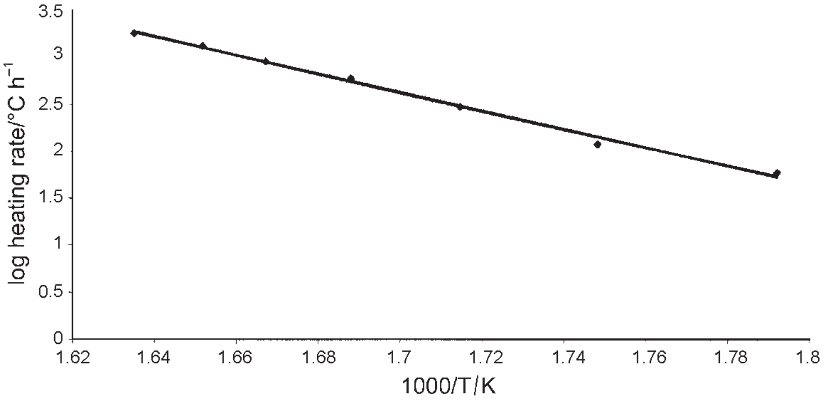


Fig. 2 Determination of the apparent activation energy of cellulose extracted from the thorns of *Ulex parviflorus*

The apparent activation energy was evaluated according to Ozawa [26] and to Audebert and Aubineau [28], using the expression

$$E=\frac{-R}{0.434}\frac{\mathrm{d}\log\beta}{\mathrm{d}(1/T)}$$

The differential term (dlogβ/(d(1/*T*)), corresponds to the slope of the straight line in Fig. 2. E=178.5 kJ mol^{-1}.

The results are presented in Table 1. The experiments were performed under an air flow 22% oxygen+78% nitrogen. We also observed, at low β, a constant proportion between the DTG peak height and β.

Table 1 Apparent activation energy of the thermogravimetric decomposition of cellulose

Origin of cellulose	Apparent activation energy (E)/kJ mol^{-1}
Flowers of *Acacia dealbata* 140595	179.5
Flowers of *Acacia dealbata* 120296	181.3
Leaves of *Quercus coccifera* 040595	188.0
Branches of *Rosmarinus officinalis* 141095	187.1
Pine cones (black, dry and not fallen in the litter) of *Pinus halepensis* 260395	190.6
Thorns of *Ulex parviflorus* 310895	187.5
Average	185.7
Sample number	6
Standard deviation	4.30
Variation coefficient/%	2.31

The DTG data presented clearly demonstrate that the mass loss and hence the thermal degradation rate depend strongly on the heating rate, as revealed by evaluating the activation energy of the mass loss process according to Freeman and Carroll [29]. The dependence of the thermal degradation, and hence of the relevant 'activation energies' on the heating rate lends support in fact to the view that the *E* value is characteristic only of the mass loss under the given heating rate conditions, but not the chemical decomposition process itself.

The average obtained for these 6 samples corresponds to the values cited in the literature [30, 31]. According to Dollimore and Hoath [32], this transformation takes place in the same way in an air flow or in a nitrogen flow. Irrespective of the pyrolysis conditions, the same low molecular mass, readily flammable products were produced [33].

Holocellulose

Holocellulose is a mixture of cellulose and hemicellulose. The study was carried out first on samples collected from different parts of a tree of *Pinus halepensis*, and then on parts of various Mediterranean plants. The thermal analysis was performed in an air or nitrogen flow.

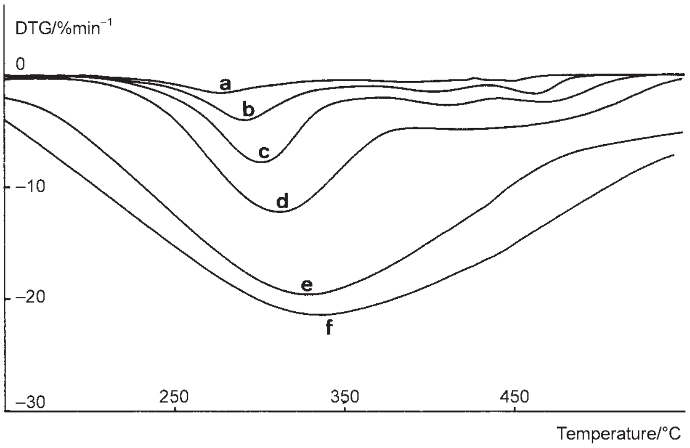


Fig. 3 DTG curves of holocellulose extracted from the new branches of *Pinus halepensis* in an air 22% oxygen flow; heating rate: *a*=2; *b*=5; *c*=10; *d*=20; *e*=50 and *f*=70°C min^{-1}

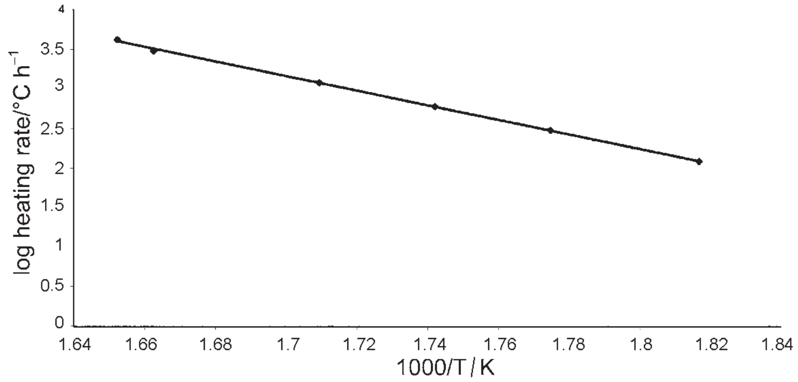


Fig. 4 Determination of the apparent activation energy of holocellulose extracted from the new branches of *Pinus halepensis*

For illustration Fig. 3 presents DTG curves obtained at different heating rates between 2 and 60°C min^{-1} for holocellulose from the new branches of *Pinus halepensis.* The resulting apparent activation energy was E=176.6 kJ mol^{-1} (Fig. 4).

The results on the holocellulose levels in several samples from a tree of *Pinus halepensis* collected on different dates, and samples of other Mediterranean plants, are presented in Table 2. The cellulose contents (in %) of the respective holocelluloses are also given.

Table 2 Apparent activation energy of the thermogravimetric decomposition of holocellulose in air flow

Samples	(Cellulose/ holocellulose)/%	App. activation energy (E)/kJ mol^{-1}
	Holocellulose samples from *Pinus halepensis*	
Old green needles 240397	75.9	181.4
New branches 240397	59.5	176.6
Old branches 040597	55.6	190.2
Old branches 040597	81.1	176.0
New brown pine cones (closed) 240397	88.6	166.1
New brown pine cones (open) 240397	89.5	167.2
Dry black pine cones in the litter 260395	96.3	169.2
Dry black pine cones in the litter 090297	100	180.5
Average	–	175.9
Sample number	–	8
Standard deviation	–	8.22
Variation coefficient/%	–	4.67
	Other holocellulose samples	
Flowers of *Acacia dealbate* 140295	43.9	162.1
Leaves of *Rosmarinus officinalis* 141095	50.7	149.3
Branches of *Rosmarinus officinalis* 141095	62.2	190.1
Leaves of *Quercus coccifera* 040595	67.9	200.8
Thorns of *Ulex parviflorus* 310895	70.5	191.2

The activation energy seemed to be independent of the cellulose level in the holocellulose from the *Pinus halepensis,* so we determined the average (m) for the 8 studied samples, 175.9 kJ mol^{-1}, with a standard deviation (SD) of 8.23 and a variation coefficient of 4.67%. The interval $m\pm2SD$ is between 159.5 and 192.3 kJ mol^{-1} for the holocellulose extracted from *Pinus halepensis* and studied in an air flow. For several samples, the activation energy was outside the interval 159.5–192.3 kJ mol^{-1} for *Pinus halepensis* holocellulose. These variations can be attributed to the chemical structures of the hemicellulose. Notwithstanding the extensive literature pertaining to the pyrolysis of cellulose, fundamental studies on hemicellulose seem to be relatively rare. The hemicelluloses contain mainly pentosan and hexosan groups [34, 35]. The data obtained for E can differ, depending on the decomposition and flammability of these. When E is high, the flammability risk is smaller (because the decomposition is slower). Conversely, if E is smaller, the flammability risk is higher.

In a nitrogen flow, the decomposition rate is lower, and consequently the activation energy is higher (Table 3). This phenomenon is due to the presence of hemicellulose.

For cellulose and holocelluloses, the apparent mechanism is of first order, as measured within our experimental set-up.

Table 3 Apparent activation energy of the thermogravimetric decomposition of holocellulose, in air and nitrogen flows

Holocellulose samples	Apparent activation energy/kJ mol^{-1}	
	22% oxygen+78% nitrogen	pure nitrogen
New brown pine cones of *Pinus halepensis* 240397	167.2	261.0
Leaves of *Rosmarinus officinalis* 141095	149.3	188.9
Thorns of *Ulex parviflorus* 310895	191.2	233.0

Lignin

It was earlier shown that the decomposition kinetics for lignin is different from the first-order kinetics observed for cellulose and holocellulose [4, 27].

Our study was carried out under three different gas flow conditions:

1. (air) mixture of 22% oxygen+78% nitrogen,
2. mixture of 6% oxygen+94% nitrogen,
3. pure nitrogen.

For lignin, we observed a correlation between the maximum mass loss rate and the heating rate. This dependence exhibits a particular form: a straight line with two slopes. For the two linear parts, we assumed two equations of the following types:

1. $Y=a_1+b_1X$ (1st part) and $Y=a+bX$ (2nd part) in air flow,
2. $Y=a_1'+b_1'X$ (1st part) and $Y=a'+b'X$ (2nd part) in 6% oxygen flow,
3. $Y=a_1''+b_1''X$ (1st part) and $Y=a''+b''X$ (2nd part) in nitrogen flow.

with Y=DTG (% min^{-1}) and $X=\beta$ (°C min^{-1}). The points of intersection of the two lines were at about

1. 5°C min^{-1} for air,
2. 1°C min^{-1} for 6% oxygen,
3. 30°C min^{-1} for nitrogen.

DTG curves for the lignin from the dry black pine cones of *Pinus halepensis* are given in Fig. 5. The heating rates used are in the interval from 1 to 60°C min^{-1}. The surrounding gas was pure nitrogen. For this sample, Fig. 6 presents the dependence of DTG (% min^{-1}) on heating rate (°C min^{-1}), in 3 different gas flows.

Table 4 reveals large variations in the slopes of the DTG *vs*. heating rate curves. Each value is specific of a plant species. For instance, the slope for the leaves of *Rosmarinus officinalis* (B-141095) is 2.5 times higher than that for the black pine cones of *Pinus halepensis* (260395).

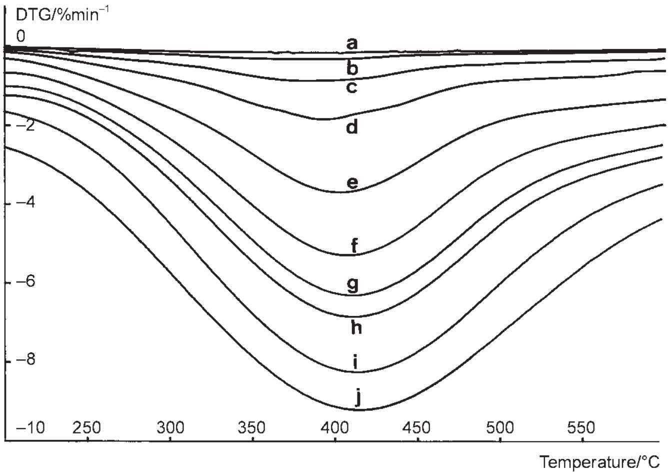


Fig. 5 DTG curves of lignin extracted from the dry pine cones of *Pinus halepensis*, in pure nitrogen flow; heating rate: a=1; b=2; c=5; d=10; e=20; f=30 g=36; h=40; i=50 and j=60°C min^{-1}

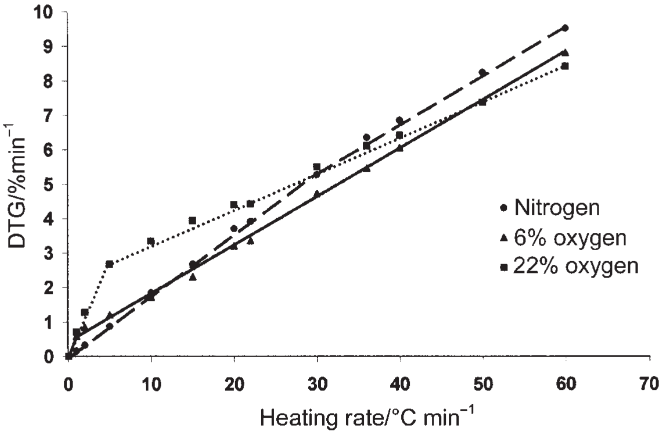


Fig. 6 Correlation between the DTG curve and the heating rate for the lignin extracted from the dry pine cones of *Pinus halepensis*, at various oxygen concentrations

This is not surprising, because the lignins have very complex chemical structures. For instance, the statistical molecular model of the Pine kraft lignin consists of 14 aromatic rings with numerous substituents [36].

The lignins decompose in the first stage by ether bond breaking, resulting in substituted phenols, which, in a second stage at high temperature, lead to charcoal.

Table 4 Results for lignins (thermal analysis in air (22% oxygen+78% nitrogen), using the expression $Y=a+bX$, with Y=DTG (% min^{-1}) and X=heating rate (°C min^{-1}), r=correlation coefficient)

Lignin samples	a/% min^{-1}	b/%°C^{-1}	r
Leaves of *Rosmarinus officinalis* A 120395	3.683	0.202	0.998
Leaves of *Rosmarinus officinalis* B 141095	2.334	0.236	0.999
Leaves of *Rosmarinus officinalis* C 141095	3.558	0.217	0.999
Leaves of *Rosmarinus officinalis* D 221198	4.608	0.187	0.995
Branches of *Rosmarinus officinalis* B 141095	2.302	0.154	0.999
Leaves and flowers of *Thymus vulgaris* 170595	3.978	0.189	0.998
Flowers of *Acacia dealbata* 140295	1.527	0.196	0.999
Leaves and small branches of *Acacia dealbata* 140295	1.992	0.196	0.997
Leaves of *Quercus coccifera* 040595	2.763	0.177	0.992
Leaves of *Quercus coccifera* 200596	1.361	0.159	0.992
Black pine cones of *Pinus halepensis* 260395	2.425	0.094	0.992
Black pine cones of *Pinus halepensis* 120296	1.527	0.116	0.998
Thorns and branches of *Ulex parviflorus* 310895	2.077	0.224	0.999
Thorns of *Ulex parviflorus* 310895	3.075	0.232	0.998

Table 5 Results for lignins (thermal analysis in a mixture of 6% oxygen+94% nitrogen, using the expression $Y=a'+b'X$, with Y=DTG (% min^{-1}) and X=heating rate (°C min^{-1}), r'=correlation coefficient)

Lignin samples	a'/% min^{-1}	b'/% °C^{-1}	r'
Leaves of *Rosmarinus officinalis* A 120395	0.116	0.307	0.999
Leaves of *Rosmarinus officinalis* B 141095	0.300	0.291	0.999
Leaves of *Rosmarinus officinalis* C 141095	0.066	0.326	0.999
Branches of *Rosmarinus officinalis* B 141095	0.266	0.201	0.998
Leaves and flowers of *Thymus vulgaris* 170595	0.546	0.254	0.997
Flowers of *Acacia dealbata* 140295	0.291	0.233	0.999
Leaves and small branches of *Acacia dealbata* 140295	0.519	0.236	0.999
Leaves of *Quercus coccifera* 040595	0.551	0.180	0.997
Leaves of *Quercus coccifera* 200596	0.196	0.174	1.000
Black pine cones of *Pinus halepensis* 260395	0.425	0.139	0.999
Black pine cones of *Pinus halepensis* 120296	0.361	0.136	0.999
Thorns and branches of *Ulex parviflorus* 310895	0.343	0.273	0.999
Thorns of *Ulex parviflorus* 310895	0.356	0.314	0.998

Table 6 Results for lignins (thermal analysis in pure nitrogen, using the expression $Y=a''+b''X$, Y=DTG (% min^{-1}) and X=heating rate (°C min^{-1}), r''=correlation coefficient)

Lignin samples	a''/%min^{-1}	b''/%°C	r''
Leaves of *Rosmarinus officinalis* A 120395	8.676	0.190	0.951
Leaves of *Rosmarinus officinalis* B 141095	4.667	0.233	0.994
Leaves of *Rosmarinus officinalis* C 141095	1.848	0.296	0.994
Leaves and flowers of *Thymus vulgaris* 170595	6.018	0.186	1.000
Leaves and small branches of *Acacia dealbata* 140295	4.610	0.193	0.993
Leaves of *Quercus coccifera* 040595	3.669	0.139	1.000
Leaves of *Quercus coccifera* 200596	1.826	0.162	1.000
Black pine cones of *Pinus halepensis* 260395	2.033	0.121	0.997
Black pine cones of *Pinus halepensis* 120296	2.253	0.113	1.000
Thorns and branches of *Ulex parviflorus* 310895	3.856	0.228	0.982
Thorns of *Ulex parviflorus* 310895	10.007	0.150	0.987

Our results indicate the following increasing sequence of lignin decomposition rate, expressed by the slope b in % °C^{-1}:

> black pine cones of *Pinus halepensis*<leaves of *Quercus coccifera*<flowers, leaves and branches of *Acacia dealbata* and leaves and flowers of *Thymus vulgaris*<thorns and branches of *Ulex parviflorus* and leaves of *Rosmarinus officinalis*.

The flammability risk increases with the mass loss rate, and the evolved gases. The *Ulex parviflorus* and the *Rosmarinus officinalis* species are well known in Provence for their action in fire starting.

A comparison of Tables 4 and 6 shows little variations in the b values, except for the thorns of *Ulex parviflorus*: b=0.232% °C^{-1} in 22% oxygen and b''=0.150% °C^{-1} in nitrogen. On the other hand, in the mixture with only 6% of oxygen, all the b values are increased, showing an increased flammability risk, even when the forests burn with a partial oxygen pressure decrease (Table 5).

* * *

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References

1 J. Kaloustian, A. M. Pauli and J. Pastor, J. Thermal Anal., 46 (1996) 1349.
2 J. Kaloustian, A. M. Pauli and J. Pastor, J. Thermal Anal., 50 (1997) 795.
3 J. Kaloustian, A. M. Pauli and J. Pastor, J. Thermal Anal., 46 (1998) 91.
4 J. Kaloustian, A. M. Pauli and J. Pastor, Acta Bot. Gallica, 145 (1998) 307.
5 R. C. Pettersen, Chemical Composition of Wood. In: The Chemistry of Solid Woods; R. M. Rowel Ed.; Advances in Chemistry Series. 207, American Chemical Society: Washington D. C., 1984; Chapter 2, p. 57.

6 TAPPI (US Technical Association of Pulp and Paper Industry) Acid Insoluble Lignin in Wood and Pulp, norm T 222 OS-74, 1974.
7 M. J. Antal and G. Várhegyi, Ind. Eng. Chem. Res., 34 (1995) 703.
8 A. D. Pouwels, G. B. Eykel and J. J. Boon, J. Anal. Appl. Pyrolysis, 14 (1989) 237.
9 A. Broido and M. A. Nelson, Combust. Flame, 24 (1975) 263.
10 A. Broido, Kinetics of Solid-Phase Cellulose Pyrolysis. In: Thermal Uses and Properties of Carbohydrates and Lignins. F. Shafizadeh, K. V. Sarkanen and D. A. Tillman, Ed.; Academic Press, New York 1976, p. 19.
11 A. G. W. Bradbury, Y. Sakai and F. Shafizadeh, J. Appl. Polym. Sci., 23 (1979) 3271.
12 D. Price, G. V. Coleman and A. R. Horrocks, J. Thermal Anal., 40 (1993) 649.
13 S. S. Alves and J. L. Figueiredo, J. Anal. Appl. Pyrolysis, 15 (1989) 347.
14 S. S. Alves and J. L. Figueiredo, J. Anal. Appl. Pyrolysis, 17 (1989) 37.
15 G. Várhegyi, M. J. Antal, P. Szabó, E. Jakab and F. Till, J. Thermal Anal., 47 (1996) 535.
16 S. Cooley and M. J. Antal, J. Anal. Appl. Pyrolysis, 14 (1988) 149.
17 G. Várhegyi, P. Szabó, W. S. L. Mok and M. J. Antal, J. Anal. Appl. Pyrolysis, 26 (1993) 159.
18 G. Várhegyi, M. J. Antal, T. Székely and F. Till, Energy and Fuels, 2 (1988) 267.
19 M. J. Antal and G. Várhegyi, Energy and Fuels, 11 (1997) 1309.
20 N. Nimour, Inflammability of Mediterranean Vegetation, Thesis from Aix-Marseille 1 University, France, 1997.
21 J. H. Flynn and L. A. Wall, J. Polymer Sci., B4 (1966) 323.
22 J. H. Flynn and L. A. Wall, J. Res. Nat. Bur. Stand., 70A (1966) 487.
23 H. E. Kissinger, Anal. Chem., 29 (1957) 1702.
24 T. Ozawa, Bull. Chem. Soc. Jpn., 38 (1965) 1881.
25 T. Ozawa, J. Thermal Anal, 2 (1970) 301.
26 M. E. Brown, Introduction to Thermal Analysis, Ed. Chapman, London 1988, Chapter 13, p. 127.
27 J. Kaloustian, A. M. Pauli and J. Pastor, J. Therm. Anal. Cal., 61 (2000) 13.
28 R. Audebert and C. Aubineau, European Polym. J., 6 (1970) 965.
29 E. S. Freeman and B. Carroll, J. Phys. Chem., 62 (1958) 394.
30 D. Davies, A. R. Horrocks and M. Greenhalgh, Thermochim. Acta, 63 (1983) 351.
31 D. L. Griffiths and R. G. Wrights, J. Anal. Appl. Pyrolysis, 8 (1985) 305.
32 D. Dollimore and J. M. Hoath, Thermochim. Acta, 45 (1981) 87.
33 R. F. Schwenker and L. R. Beck, J. Polym. Sci. Part C, 2 (1963) 331.
34 M. Rinaudo, Revue française Corps Gras, 22 (1975) 429.
35 N. Shukry, B. S. Girgis and M. Z. Sefain, Bul. Soc. Chim, F, 127 (1990) 515.
36 R. A. Fenner and J. O. Lephardt, J. Agric. Food Chem., 29 (1981) 846.