

DECOMPOSITION OF BIO-POLYMERS OF SOME MEDITERRANEAN PLANTS DURING HEATING

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Abstract

Forest fires are a plague for all countries in the world. Many factors can induce them. The organic matter ('fuel') in the plant, is often responsible for the start of the fire. The bio-polymers and mainly the cellulose decompose at about 300°C with flammable evolved gas. This decomposition is first order, and the activation energy is about 180 kJ mol⁻¹. On the other hand, the degradation of the lignin seems more complex, but we observed on many samples, a linearly decomposition of the lignin vs. the heating rate (in the interval close to the start of the forest fire, 300 to 3000°C h⁻¹). The decomposition of the plant during the heat is mainly dependent on the cellulose level. This degradation is also slightly dependent on the lignin level mainly if the lignin present in this plant is less stable.

Keywords: cellulose, decomposition, kinetic, lignin, thermogravimetry

Introduction

The risk prevention of forest fires is based on several factors: the initiator agent (mainly from human origin), the fuel (depending on the chemical composition of vegetals, therefore on the flammable evolved gas in the case of pyrolysis), the accelerating agent (wind) and the fire retardants (rain and fireproofs poured in case of fire).

In an earlier study, we have determined the chemical composition of the plants and their thermal behaviour. We measured the evolution of water at about 70, a first exothermic peak at about 300 and a last one between 380 and 440°C, by differential thermal analysis (DTA), realized on freshly cut plants. The first exothermic peak is due to ignition of flammable evolved gas, the last one to the combustion of the residual char remaining [1].

Then we have determined the most important compounds by analytical procedures: cellulose, holocellulose, lignin, essential oil, mineral ashes and extractives by the 2:1 volume mixture benzene-ethyl alcohol. We observed a good correlation between the maximal decomposition rate at about 300°C and the cellulose content [2]. Thermal analysis was performed with a heating rate of 120°C h⁻¹ from the ambient temperature to 650°C, under air sweeping (0.5 L h⁻¹). In the forest fire, the spreading

rate of the heat often goes beyond $120^{\circ}\text{C h}^{-1}$. Is the correlation presented before valid in all cases? We will try to answer this question.

What we are describing in this papers is the observed thermal behaviour, first, on six samples of plants (the chemical determination has been made) with 60 to $3000^{\circ}\text{C h}^{-1}$ heating rate, then on cellulose and lignin issued from these samples.

Experimental

Samples – Apparatus – Procedure

We gathered the plants in Marseilles and its periphery:

- *Ulex parviflorus* (gorse of Provence);
- *Quercus coccifera* (kermes oak);
- *Acacia dealbata* (mimosa);
- *Pinus halepensis* (Pine of Aleppo);
- *Rosmarinus officinalis* (rosemary).

Chemical analyses were made [3], on aerial parts: leaves, branches, flowers and fruits.

First, we determined the essential oil on a part of the freshly picked plants (according to the French Pharmacopea). Another part was dried at 110°C in about fifteen hours with the determination of the mass loss. Then the samples were ground and sifted. The powder is accepted by the 1 mm-side sieve. We determined on these powders:

- the mineral ashes obtained after one h at 650°C ;
- the cellulose, by gravimetry, after reaction with a reactive mixture: ethyl alcohol-nitric acid (4V–1V); [4]
- the extractives with a benzene ethyl alcohol mixture (2V–1V) with Soxhlet apparatus [5].

On the powder residues obtained after the Soxhlet method, we calculate the lignin and the holocellulose. The lignin was analysed by gravimetry after attack by 24.0 N sulfuric acid [5]. Holocellulose (*i.e.* cellulose+hemicellulose) was also analysed by gravimetry after reaction of the powder with sodium chlorite in acetate buffer at pH 4.9 [4].

Thermal analysis was ran on a simultaneous DTA–DTG instrument (Setaram 92) with platinel thermocouples, heating rate of 60 to $3000^{\circ}\text{C h}^{-1}$ from ambient temperature to 800°C , with 0.5 L h^{-1} nitrogen sweeping or with the mixtures: nitrogen 94 – oxygen 6, or nitrogen 78 – oxygen 22%. The sample mass was between 20 and 30 mg, the crucibles were platinum, and kaolin was applied as inert thermal reference material.

Kinetic decomposition of six powder samples

In this contribution we have chosen to present only the results from the six samples of plants picked between February 1995 and February 1996. The cellulose content in these samples was between 14 and 52% of the dry matter (DM).

A (14-02-95) and A' (12-02-96) – flowers of *Acacia dealbata*;
 B (14-10-95) – leaves of *Rosmarinus officinalis*;
 C (04-05-95) – leaves of *Quercus coccifera*;
 D (14-10-95) – branches of *Rosmarinus officinalis*;
 E (31-08-95) – thorns of *Ulex parviflorus*;
 F (26-03-95) – pine-cones of *Pinus halepensis* (formed in 1994, dry sample but not fallen).

In Table 1 we present the chemical analysis results (towards the dry matter) of these powders.

Table 1 Chemical determination of the six powders of plants (Mass % of dry matter=%/DM)

Samples (%/DM)	A	B	C	D	E	F
Cellulose	14.3	15.3	24.5	35.2	38.8	52.0
Lignin	47.9	24.4	28.5	30.1	25.6	35.9
Holocellulose*	32.6	30.2	36.1	56.6	55.0	54.0
Hemicellulose	18.3	14.9	11.6	21.4	16.2	2.0
Extractives	10.1	25.3	9.85	4.15	9.39	9.15
Essential oil**	0	3.01	0	0.085	0	0.32
Ashes	4.85	6.42	4.42	3.94	2.21	0.61
Sum of the determined compounds	95.5	89.3	78.9	94.9	92.2	100

*Holocellulose=cellulose+hemicellulose

**In ml/100 g dry matter

A – flowers of *Acacia dealbata*; B – leaves of *Rosmarinus officinalis*;

C – leaves of *Quercus coccifera*; D – branches of *Rosmarinus officinalis*;

E – thorns of *Ulex parviflorus*; F – pine-cones of *Pinus halepensis*

The sum of the different components is between 78.9 and 100%/ DM.

The result of lignin in sample A seems to be too high; this is probably due to the stalks gathered with the flowers.

Thermal analysis was made with these six samples. We will only mention in Table 2, the maximum decomposition rate at about 300°C (%/min) for each sample. We also computed the linear regression equations $Y=a+bX$ with Y =maximum decomposition rate of the powders (%/min), X =cellulose (%/DM), and r =correlation coefficient.

We first observe, that 0.9587 is the highest r value (very high significance) for 120°C h⁻¹ heating rate, and 0.8142 is the smallest r value (significance) for 1800°C h⁻¹.

Then, we looked for a probable influence of the components: cellulose and lignin, on the kinetic decomposition in the case of high heating rates.

Table 2 Maximum decomposition rate (%/min) vs. heating rate ($^{\circ}\text{C h}^{-1}$), for the six powders of plants

Heating rate/ $^{\circ}\text{C h}^{-1}$	A	B	C	D	E	F	<i>a</i>	<i>b</i>	<i>r</i>	Significance level/%
60	0.71	0.62	0.80	0.95	0.88	1.38	0.3822	0.01692	0.9308	9<1 HS
120	1.36	1.22	1.56	1.95	1.80	2.65	0.7507	0.03351	0.9587	<0.1 VHS
300	3.50	3.11	3.39	4.83	4.67	5.30	2.3821	0.05834	0.9434	<1 HS
600	5.79	5.40	5.65	8.27	8.45	8.77	4.0503	0.1001	0.9245	<1 HS
900	7.28	7.63	7.50	10.91	10.94	10.40	5.9680	0.1047	0.8504	<5 S
1320	9.07	9.85	9.75	13.59	13.81	13.01	7.7257	0.1262	0.8528	<5 S
1800	10.81	11.86	11.67	16.07	15.80	14.81	9.6495	0.1284	0.8142	<5 S

S=significance; HS=high significance; VHS=very high significance
A – flowers of *Acacia dealbata*; B – leaves of *Rosmarinus officinalis*;
C – leaves of *Quercus coccifera*; D – branches of *Rosmarinus officinalis*;
E – thorns of *Ulex parviflorus*; F – pine-cones of *Pinus halepensis*

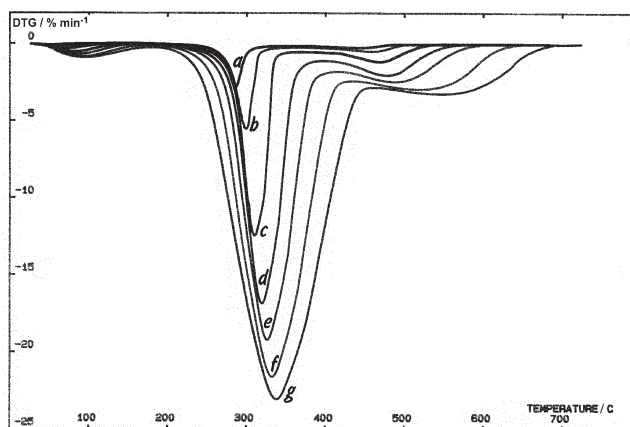


Fig. 1 DTG curves of cellulose extracted from sample E (thorns of *Ulex parviflorus*) air (oxygen 22 – nitrogen 78%) sweeping; heating rate=60 (a); 120 (b); 300 (c); 600 (d); 900 (e); 1320 (f); 1800° h⁻¹ (g)

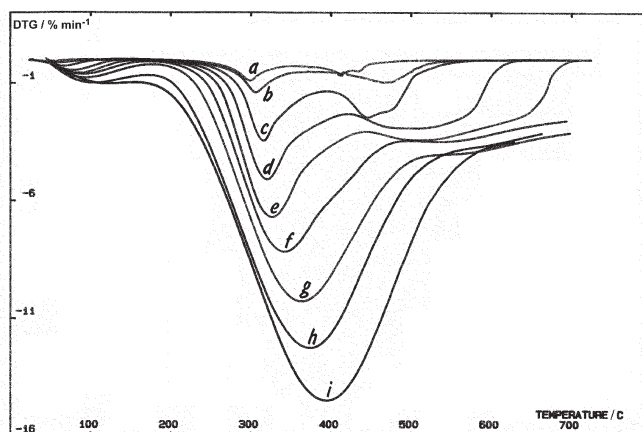


Fig. 2 DTG curves of lignin extracted from sample E (thorns of *Ulex parviflorus*) air (oxygen 22 – nitrogen 78%) sweeping; heating rate=60 (a); 120 (b); 300 (c); 600 (d); 900 (e); 1320 (f); 1800 (g); 2400 (h) and 3000°C h⁻¹ (i)

Kinetic decomposition of cellulose and lignin

Cellulose and lignin were separated from the plants according to the methods presented before.

Figures 1 and 2 show DTG curves for cellulose and lignine from sample E (thorns of *Ulex parviflorus*). In Fig. 3, the maximum decomposition rate is plotted vs. the heating rate, both for cellulose and lignine. The shape seems different: cellulose corresponds with an exponential curve, while lignine can be described with two straight lines with different slopes (the first from 0 to about 350°C h⁻¹, and the second from 350 to 3000°C h⁻¹).

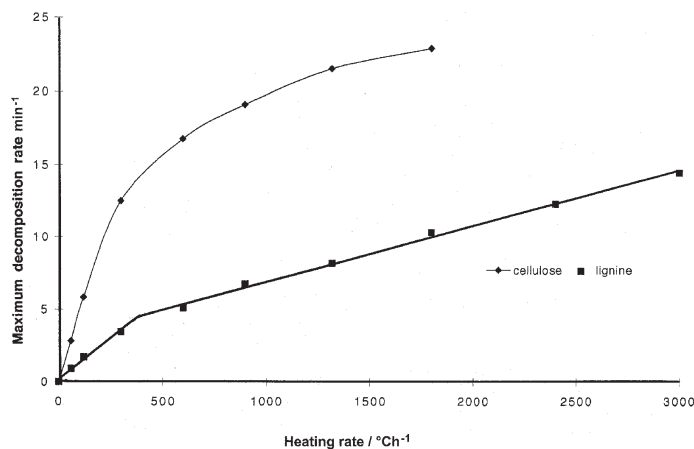


Fig. 3 Maximum decomposition rate of cellulose and lignin vs. heating rate (sample E – thorns of *Ulex parviflorus*), air (oxygen 22 – nitrogen 78%) sweeping

Cellulose

Cellulose is often lightly hydrated. It is transformed into levoglucosan which decomposes to volatiles. It is possible to calculate, for this main phenomenon, the activation energy (E_a) during pyrolysis of the cellulose if we assume a first order decomposition. Two methods can be used: parallels [6] and T_{\min} (Kissinger plot) [7].

For the parallels method, first, we determine for different heating rates β , the temperature T (K), at which a specific constant mass loss is reached. Plotting of $\log\beta$ vs. $1/T$ gives E_a , according to the equation:

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

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

with R =perfect gas constant= $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

The differential term $d\log\beta/d(1/T)$ corresponds to the slopes of the different lines: $-9.1767 \cdot 10^3$ for 20% mass loss; $-9.4989 \cdot 10^3$ for 30; $-9.6170 \cdot 10^3$ for 40; $-9.6140 \cdot 10^3$ for 50 and $-9.3933 \cdot 10^3$ for 60%. From the average of these five values, we deduce $E_a=181.2 \text{ kJ mol}^{-1}$.

For the T_{\min} method, the temperature T_{\min} , belonging to the peak of DTG curve, is determined. We determine E_a like before, by plotting $\log\beta$ vs. $(1/T_{\min})$

$$E_a=187.6 \text{ kJ mol}^{-1}$$

The results for the six plants are contained in Table 3. Experiments were made under air sweeping. The sample E was also performed under nitrogen and the mixture oxy-

gen 6 – nitrogen 94%. The decomposition of cellulose seems to be independent on the nature of the surrounding gas. It is well known that cellulose firstly reacts into levoglucosan and then decomposes. This transformation takes place as well in air as in nitrogen sweeping [8], and is independent of the nature of the surrounding gas, since it is a solid \leftrightarrow solid reaction. When the second step: levoglucosan + O₂/N₂ \rightarrow decomposition products, is faster than the first solid \leftrightarrow solid reaction, then this first step is rate determining and is not influenced by the composition of the surrounding gas phase.

Table 3 E_a of cellulose

Cellulose	$E_a/\text{kJ mol}^{-1}$	
	Parallels method	T_{\min} method
A	178.7	179.5
A'	176.9	181.3
B	201.1	229.3
C	178.3	188.0
D	184.4	187.1
E oxygen 22%	181.2	187.6
E oxygen 6%	184.0	180.5
E oxygen 0%	177.9	175.6
F	184.9	190.6
Average	180.8	183.8
Standard deviation	3.26	5.23
Variation coefficient/%	1.80	2.84

The cellulose extracted from the sample B is not pure, because we observed on DTG curve, a shoulder at about 250°C. Thus, we did not use its values in the computing of averages.

We obtain a better reproducibility in case of the parallels method (180.8 kJ mol⁻¹ and variation coefficient 1.80%). The values obtained for E_a are comparable with literature values (165.0 to 175.6 kJ mol⁻¹ according to Davies and Horrocks [9], Griffiths and Wright [10]).

Lignin

The particular form (linear with two slopes) of the variation of the maximum decomposition rate vs. heating rate, appears also for all studied plants. We computed the parameters a_1 , b_1 and a_2 , b_2 according to the straight lines, besides the correlation coefficient (Table 4).

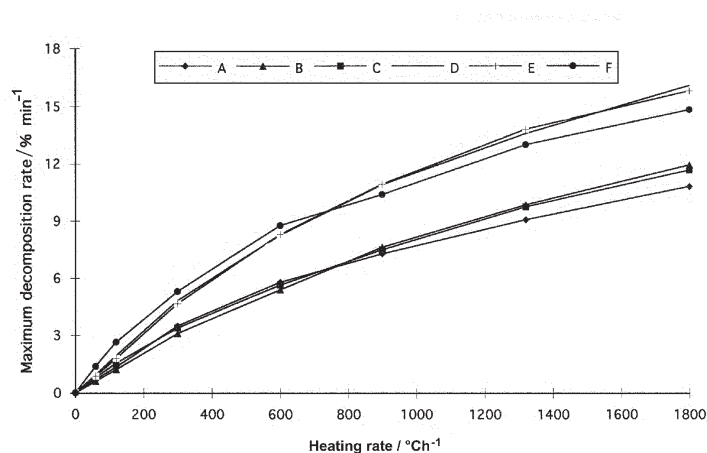


Fig. 4 Maximum decomposition rate vs. heating rate
 A – flowers of *Acacia dealbata*; B – leaves of *Rosmarinus officinalis*;
 C – leaves of *Quercus coccifera*; D – branches of *Rosmarinus officinalis*;
 E – thorns of *Ulex parviflorus*; F – pine-cones of *Pinus halepensis* air (oxygen
 22 – nitrogen 78%) sweeping

Table 4 Equations of the regression straight lines computed from the maximum decomposition rate (%/min) vs. the heating rate (°C h⁻¹) of lignins

Samples	First part $Y=a_1+b_1X$			Second part $Y= a_2+b_2X$			Significance level/%
	a_1	b_1	r	a_2	b_2	r	
A	-0.0042	0.7875	1.000	1.527	0.1959	0.999	< 0.1 VHS
B	-0.0443	1.165	0.998	2.334	0.2558	0.999	< 0.1 VHS
C	-0.0085	0.6005	1.000	2.763	0.1766	0.992	< 0.1 VHS
D	0.0557	0.4571	0.999	2.302	0.1544	0.999	< 0.1 VHS
E	0.1618	0.6729	0.994	3.075	0.2317	0.998	< 0.1 VHS
F	0.0142	0.6575	0.999	2.425	0.0994	0.992	< 0.1 VHS

VHS=very high significance

A – flowers of *Acacia dealbata*; B – leaves of *Rosmarinus officinalis*;
 C – leaves of *Quercus coccifera*; D – branches of *Rosmarinus officinalis*;
 E – thorns of *Ulex parviflorus*; F – pine-cones of *Pinus halepensis*

We observe large differences between the b_1 and b_2 values. For instance, b_1 of B is twice and a half bigger than b_1 of D. The same phenomenon is observed for b_2 of B and b_2 of F. This is not surprising because the lignins have very complex chemical structures, (for instance the statistic model of the Pine Kraft lignin consists of 14 aromatic rings with numerous substituents [11]).

Discussion and conclusion

Figure 4 shows the curves of the decomposition rates vs. the heating rate for the six plants.

We indeed note a similarity between A, B and C (respectively 14.3, 15.3; and 24.5%/DM, of cellulose) in case of heating rate lower than about $600^{\circ}\text{C h}^{-1}$. On the other hand, at about $1800^{\circ}\text{C h}^{-1}$, A has the lowest value, probably because A contained a high level of lignin (47.9%/DM).

Also the curves from D, E and F show some resemblance. We see that F has a higher rate at low heating rates and the lowest decomposition rate at high heating rates. This is caused by the high cellulose content (52%/DM), giving high decomposition rates at low heating rates, and the high lignin content (35.9%/DM), giving lower decomposition rates at high heating rates.

In conclusion, in case of fire forest with a very weak spreading heat the ease of ignition can be valued according to the maximum decomposition rate, i.e. the cellulose level. But on the other hand, when spreading heat is very high, for instance $1800^{\circ}\text{C h}^{-1}$, the decomposition rate depends on the presence of the lignin in the powder of the plant. The low decomposition kinetic parameter (b_2 at about 0.099) can decrease the decomposition rate of the powder. On the other hand, a high value of b_2 (for instance 0.25) can increase this decomposition, and favour the flammability of the plants.

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References

- 1 J. Kaloustian, A. M. Pauli and J. Pastor, *J. Therm. Anal.*, 46 (1996) 1349.
- 2 J. Kaloustian, A. M. Pauli and J. Pastor, *J. Therm. Anal.*, 50 (1997) 795.
- 3 B. Monties (ed.), *Les Polymères végétaux*, Gautier-Villars, Paris (1980).
- 4 R. C. Pettersen, In *Chemistry of solid woods; Chemical composition of wood*, ed. R. M. Rowell, *Advances in chemistry series – American Chemical Society, Washington D.C.* (1984) Chap. 2.
- 5 Tappi (Technical Association of Pulp and Paper Industry); *Acid-insoluble lignin in wood pulp*; T 0222 OS-74 (1974).
- 6 R. Audebert and C. Aubineau, *Europ. Polym. J.*, 6 (1970) 965.
- 7 T. Ozawa, *J. Therm. Anal.*, 2 (1970) 301.
- 8 D. Dollimore and J. M. Hoath, *Thermochim. Acta*, 45 (1981) 87.
- 9 D. Davies and A. R. Horrocks, *Thermochim. Acta*, 63 (1983) 351.
- 10 D. L. Griffiths and R. G. Wright, *J. Anal. Appl. Pyrolysis*, 8 (1985) 305.
- 11 R. A. Fenner and J. O. Lephardt, *J. Agric. Food Chem.*, 29 (1981) 846.