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Thermochimica Acta 401 (2003) 77–86

thermochimica acta

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Chemical and thermal analysis of the biopolymers in thyme (*Thymus vulgaris*)

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Received 24 July 2002; accepted 26 September 2002

Abstract

Thyme (*Thymus vulgaris*) has been known, long time ago, for its aromatic properties. It contains essential oils and polymers such as cellulose (mixture of hemicellulose and cellulose) and lignin. The thyme, studied in this work, was gathered from the same place, in the period from November 1999 to October 2000. The chemical analysis (water, total ash, essential oils, extractive substances, cellulose, holocellulose and lignin) can be used roughly in the characterisation of the four periods that correspond to the four seasons of the year. The cellulose level was found to be more than lignin level in the wet periods (growth of the plant). The opposite was found in the dry periods. The total ash and essential oil levels were found to be high during the period of high pluviometry. The thermal decomposition of cellulose and holocellulose was found to fit well with the first-order kinetics. The activation energy, under air flow, was 185 and 196 kJ mol^{-1} for cellulose and holocellulose, respectively. The maximum decomposition rate and thermal analysis heating rate of lignin were found to have a direct linear relationship.

Keywords: Thyme; Thermal analysis; Chemical analysis; Cellulose; Holocellulose; Lignin

1. Introduction

Thyme is a very popular aromatic plant in Provence. It has been known for its aromatic properties. It is always present in a wild state in plains and hills, like lavender, rosemary, sage and many other wild plants. It contains essential oils that can be used medicinally. The polymers present in thyme, such as, cellulose, holocellulose (mixture of cellulose and hemicellulose) and lignin, can increase the risk of fire in forest of Provence. The fire risk has been cited in several recent publications [1–5]. Thyme is considered to be an important factor for the spreading of fire due to the presence of essential oils, flammable volatile substances present in cellulose [6–14] (numerous oxygenated compounds, such as, alcohols, carbonyls and carboxylic acids [C_1–C_4]), hemicellulose [12] (mainly oses) and lignin [12] (substituted phenols). It was observed that divided wood, under pyrolysis and partial combustion, produced volatile substances, oils and char. The principal products were water and carbon dioxide, besides, partially oxidised products such as carbon monoxide, methane and other volatile flammable compounds [12].

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PII: S0040-6031(02)00569-5

The ignition of Mediterranean plants in forest fires leads to the volatilisation of flammable volatiles, such as, essential oils and/or evolved gases. This resulted from the decomposition of less volatile components (biopolymers), such as, cellulose, holocellulose and lignin. Essential oil represents only a few milliliter for 100 g of dry plants, while cellulose content can range from 20 to 50% in the dry plant. For this reason, cellulose and other biopolymers pyrolisis kinetics, are currently a topic of great interest.

This work aimed at the use of thermal analysis techniques to determine the decomposition kinetics of these biopolymers.

2. Experimental

- Wild thyme (*Thymus vulgaris*) was gathered from the same area, near the town of Gemenos (Department of Bouches du Rhone), between November 1999 and October 2000.
- The essential oil in a part of the freshly gathered plant was determined, according to the European Pharmacopoeia (1997 and 2000). A sample of about 50 g (weighed accurately) was put in a 1000 ml flask with 500 ml of bidistilled water and distilled for 5 h.

  Another part of the plant was dried at 110 °C for 15 h using the weight loss determination. This weight loss determination at 110 °C corresponds, approximately, to the weight loss desiccation (i.e. to make drying of the sample until getting a constant weight). Indeed, we compared the results of the weight loss at 110 °C and azeotropic distillation of water, in the same samples, which gave nearly the same results. For example in three different samples, heating weight losses at 110 °C, performed on 1 g of the sample, were 51.0, 29.7 and 7.99%. For water determination by azeotropic distillation with toluene, performed on 25 g of the sample, the results were 51.2, 30.3 and 8.08%, for the samples, respectively.

  The samples were then powdered and sieved, so, homogeneous samples were obtained. On these powders the following were determined: total ash (TA) obtained by heating at 650 °C for 1 h in air, cellulose by gravimetry after the action of HNO_3:EtOH (1:4) [15] and the extractives by C_6H_6:EtOH (2:1) using Soxhlet apparatus [16].

  Lignin and holocelluose were determined on the residue remained after Soxhlet extraction method. Lignin was analysed by gravimetry after the reaction with 24N H_2SO_4 [16]. Holocellulose was also determined by gravimetry after the reaction of the powder with sodium chlorite in acetate buffer (pH 4.9) [15]. Hemicellulose was determined from the difference between holocellulose and cellulose. All results were expressed as percentage in the dry matter (%/DM).

  The results of chemical analysis, cf. Section 3, are valid only for these samples, because several other different samples of thyme harvested elsewhere, in the same period, gave different results due to the different kind of soils, precipitations and chemotypes.

  Earlier, the reproducibility of the different chemical analysis methods was performed on a sample of rosemary [1]. The relative standard deviation (R.S.D.) values were about 2% for gravimetry and 5% for extraction and distillation. The results (%/DM (R.S.D.%)) were as follows: 6.33 (1.97), 35.4 (2.03), 33.9 (2.18), 55.0 (1.78) and 20.0 (4.80), for total ash, cellulose, lignin, holocellulose and extractives, respectively. The result for essential oil was 1.95 ml/100 g DM with R.S.D. value of 5.54%.
- Thermal analysis was run on differential thermal analysis (DTA)–thermogravimetry (TG) simultaneous apparatus (Setaram 92, Scientific and Industrial Equipment, France). A mode isothermal was held at 25°C during 5 min, then a heating rate of 1–60 °C min^{-1} up to 800°C. Runs were done in reconstituted air flow: 22% oxygen and 78% nitrogen. Volumetric flow rate was 0.5 l h^{-1}, measured at ambient temperature and atmospheric pressure (about 0.022 mol h^{-1} as molar flow). Sample mass, weighed accurately, of about 20–30 mg, was put in a platinum crucible of 100 μl capacity. Pyrolysed kaolin was used as an inert thermal reference in DTA. Tests were done on freshly cut samples (about 1–3 mm) and on powders dried at 110 °C (less than 1 mm size). Indium, tin, lead and aluminium, all above 99.9% of purity, were used, as standards, for DTA and TG temperature calibration. Weight loss was calibrated in TG by calcium oxalate monohydrate standard. Platinel* thermocouples were used in temperature determination.

Table 1
Sampling data

Period	Climatology, precipitation	Batch	Gathering date	WLdes (%)[a]	Cel/Lig[b]
1st	Very damp; 110 mm in November and 35 mm in December; slight growth	1	23 November 1999	58.7	1.11
		2	6 December 1999	58.6	1.20
		3	20 December 1999	61.2	1.21
		4	3 January 2000	64.7	1.19
2nd	Dry and cold; 2 mm in January; end of growth	5	17 January 2000	59.4	0.74
		6	31 January 2000	47.9	0.93
		7	14 February 2000	58.1	0.87
3rd	Very damp; 41 mm in March and 100 mm in April; growing and flowering since April	8	28 February 2000	59.1	1.03
		9	13 March 2000	57.8	1.20
		10	27 March 2000	61.3	1.00
		11	14 April 2000	63.6	1.05
		12	25 April 2000	66.6	1.05
		13	9 May 2000	69.1	1.12
4th	Dry; severe forest fires in Provence and in Corsica; stopping of growth	14	22 May 2000	64.0	0.78
		15	19 June 2000	55.4	0.77
		16	3 July 2000	45.4	1.00
		17	17 July 2000	44.5	0.75
		18	28 August 2000	22.2	0.76
5th	Similar to the 1st period	19	17 October 2000	61.3	1.08

[a] Weight loss desiccation.
[b] Cellulose/lignin ratio.

3. Results and discussion

3.1. Chemical analysis

Table 1 shows the sampling data (batch, gathering date, period and climatological conditions). The cellulose/lignin ratio will be explained later. From the weight loss of water at 110 °C, the samples can be divided to four groups corresponding to four periods. These four periods correspond roughly to the four seasons of the year. The last sample of 17 October 2000 (batch 19) would be linked with the 1st period, even if it had been gathered about 1 year later.

Table 2 shows the chemical results of each gathered sample from November 1999 to October 2000.

After harvesting, samples were kept in hermetically closed bags, for 1 h, before coming to the laboratory. Weight loss was determined by heating the sample at 110 °C for 15 h. After a storage period of 10 days, at room temperature and in air, a weight decrease by 8% was observed. This value was lower than that obtained with other previously studied plants, such as, *Pinus halepensis*, with brown needles (12.0%), dry black cones fallen in the litter (16.8%), brown cones opened on the tree (13.3%) and barks of a dead tree (12.7%) [17]. So, thyme may offer a higher risk for forest fires than others, due to the low water content in the cut plant and in the sample division (small branches).

The mean, standard deviation (S.D.) and relative standard deviation (R.S.D.), computed from 19 different samples, are listed in Table 2. It should be noted that the samples were collected in the same place, but in different periods of the year, so, they do not belong, exactly, to the same population in a statistical sense. The sum of each determined component was 79%/DM. The density of thyme oil is between 0.90 and 0.95, so, the sum from the average values would be very slightly decreased (about 0.2%). This sum varies from about 70–90%. Several components, present in low levels, were not determined, such as, nitrogen containing compounds (aminoacids, proteins), oses (free or complexed), organometallic compounds with calcium and magnesium, etc.

Variations of the results, according to the aerial parts, were observed. For example, in sample 10, leaves, branches and flowers were divided and

Table 2
The chemical results of different samples of thyme gathered in the same place from November 1999 to October 2000

Batch	WLdes[a] (%)	EO[b](ml/%DM)	TA[c] (%/DM)	Ext[d] (%/DM)	Cel[e] (%/DM)	Lig[f] (%/DM)	Holocel[g] (%/DM)	Hemice[h] (%/DM)
1	58.7	1.95	5.29	11.2	28.9	26.0	42.1	13.2
2	58.6	2.53	5.90	14.4	28.7	23.9	38.1	9.4
3	61.2	2.67	5.66	15.0	28.0	23.1	32.5	4.6
4	64.7	2.12	5.92	13.9	27.7	23.2	31.8	4.2
5	59.4	2.18	5.51	11.5	17.7	25.6	35.5	17.8
6	47.9	1.71	5.41	13.1	21.0	22.7	37.7	16.7
7	58.1	2.35	7.13	10.2	20.8	24.0	32.1	11.3
8	59.1	2.16	5.34	9.9	23.7	22.9	31.4	7.7
9	57.8	2.13	5.95	10.4	24.7	20.5	30.6	5.9
10	61.3	1.97	6.01	9.0	20.4	20.4	38.1	17.7
11	63.6	2.37	5.98	10.5	21.9	20.9	35.8	13.9
12	66.6	2.85	6.79	11.2	21.5	20.5	33.6	12.1
13	69.1	3.41	7.00	12.6	20.9	18.7	36.1	15.2
14	64.0	3.00	6.43	13.1	19.4	25.0	31.6	12.2
15	55.4	2.53	5.98	9.8	19.9	26.0	30.8	10.9
16	45.4	2.52	5.63	11.4	24.0	23.9	32.8	8.8
17	44.5	1.78	4.77	9.2	19.0	25.4	43.1	24.1
18	22.2	1.87	4.96	7.5	22.4	29.5	47.4	25.0
19	61.3	1.89	5.89	10.5	27.9	25.8	40.0	12.1
Mean	56.78	2.32	5.87	11.28	23.08	23.58	35.85	12.78
S.D.	10.67	0.448	0.631	1.97	3.60	2.62	4.73	5.76
R.S.D.%	18.8	19.4	10.8	17.5	15.6	11.1	13.2	45.1

The results are the average of two to three tests done on the whole plant.

[a] Weight loss desiccation at 110 °C for 15 h.

[b] Essential oil.

[c] Total ash at 650 °C in air.

[d] Extractives.

[e] Cellulose.

[f] Lignin.

[g] Holocellulose.

[h] Hemicellulose, S.D., standard deviation; R.S.D., relative standard deviation.

weighed separately. The distribution (% w/w) was 70.6, 21.6 and 7.8% for leaves, branches and flowers, respectively. Weight loss desiccation (WLdes) and total ash (TA) were determined for these separate parts. The % WLdes (TA, %/DM) were 62.9 (6.32%/DM), 49.2 (4.33%/DM) and 79.5% (8.69%/DM) for leaves, branches and flowers, respectively. The amount of WLdes and TA, in the whole plants, was mainly due to leaves (high weight fraction of leaves in the plant, high amount of water and total ash in leaves).

It was observed earlier [2] that cellulose and lignin were present in high levels in the branches. In this study, it has been observed that cellulose was found to be in a high amount in the growth period of the plant. Lignin content increased by ageing. The 1st and 3rd periods correspond to the growth (Table 1) as shown by extension of branches, appearance of leaves and flowers. The value of cellulose/lignin ratio was higher than 1. On the contrast, the 2nd and 4th periods are characteristic for dryness and the value of cellulose/lignin ratio was lower than 1.

Fig. 1 shows a linear correlation between essential oil (EO) and total ash (TA) as deduced from Table 2. The equation is:

$$\mathrm{EO(ml/\%DM)} = 0.50\mathrm{TA(\%/DM)} - 0.63$$

$$[w = 19;\ r = 0.707 \text{ and } P < 0.001]$$

This equation is valid for the following ranges: 4.77–7.13%/DM of TA; 1.71–3.41 ml/%DM of EO,

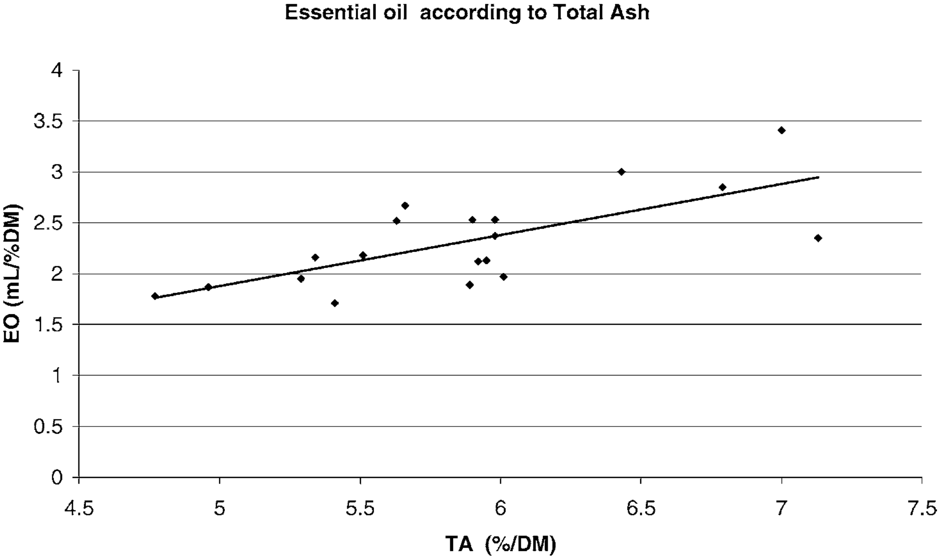

Fig. 1. Variation of essential oil (Y, ml/100 g DM) according to total ash (X, %/DM) ($Y = 0.5020\ X - 0.6318$; with $w = 19$ and $r = 0.707$).

for the samples gathered in the same area. The photosynthesis of leaves, thanks to chlorophyll and minerals, could explain the formation of oil. So, essential oil increases by the presence of total ash and this could favour the flammability risk. The low level of water, the presence of organic extractives, hemicellulose and biopolymers can also increase this risk. Cellulose, holocellulose and lignin produce flammable volatiles. These flammable volatiles start to show at 200 °C and the maximum peak of DTG and DTA appears at 300 °C [18].

3.2. Thermal analysis

3.2.1. Freshly gathered thyme and dried powdered samples

The thermal analysis can be a useful tool in the fire risk estimation [18–20]. The simultaneous thermal analysis DTA–TG was run using the fresh plant and its different aerial parts, the dried powdered samples and the isolated components, such as, extractives, essential oil, cellulose, holocellulose and lignin. The end of the stalk was analysed and characterised by three stages with weight loss, under air flow, as follows:

- until about 140 °C, water volatilisation (endothermic reaction),
- between 140 and 380 °C, decomposition of the biopolymers with char formation (exothermic reaction),
- between 380 and 500 °C, char combustion (exothermic reaction).

The second stage is considered to be of high interest in the estimation of the fire risk due to the decomposition of the wooden biopolymers. An example of such analysis is given in Fig. 2. Under nitrogen, the endothermic peak of water volatilisation was well observed by DTA. The absence of other well characteristic endothermic peaks could be explained by the absence of oxidation products that obtained under air.

The results, presented in Table 3, show the three stages of thermal analysis: water loss, thermal decomposition and combustion of char. In TG experiment, the measured weight loss is corresponding to the thermal decomposition of biomass components. The combustion of volatiles occurs, consecutively, in the gas phase and, obviously, TG cannot measure it. The study was done on the whole fresh plant, each aerial part (leaves, branches and flowers) and dried powdered samples. The temperature at the maximum of DTA and DTG peaks (T_{max}, °C), and % weight loss at about 140 °C (moisture) and at about 500 °C (total volatilised mass), are determined. The volatilisation

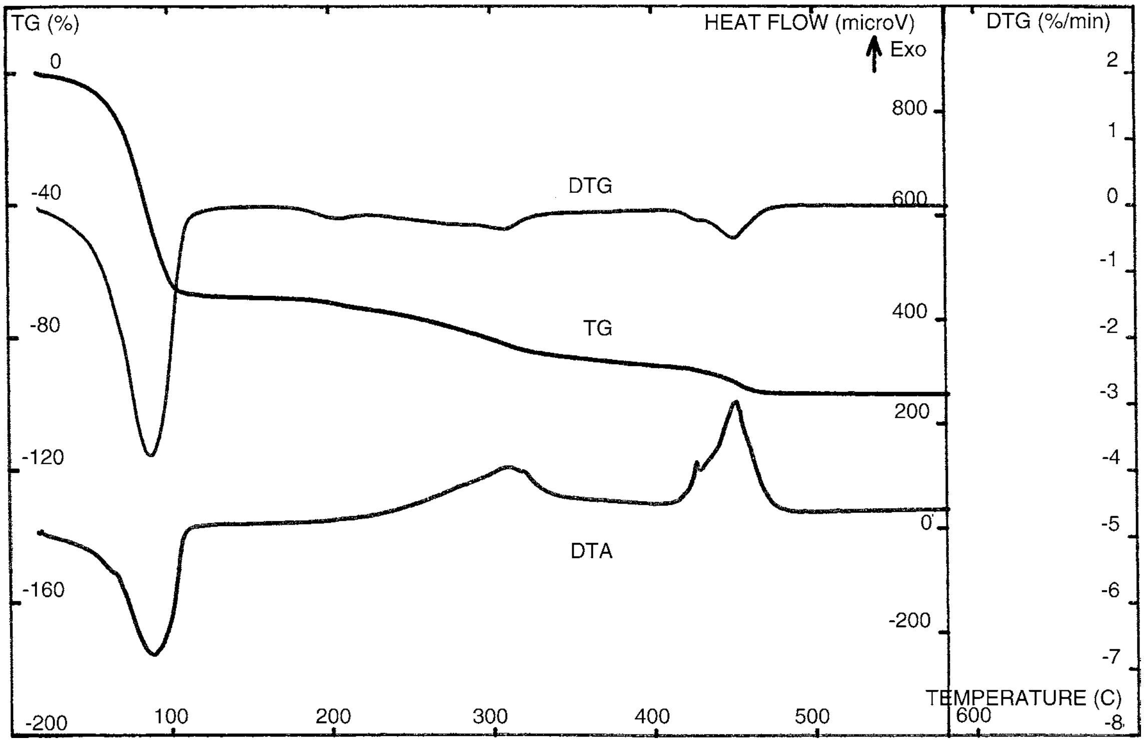

Fig. 2. TG, DTG and DTA curves of a freshly gathered thyme (sample weight 32.2 mg, heating rate 2 °C/min, air flow (22% oxygen–78% nitrogen) 0.5 l/h, endothermic DTA and DTG peaks (88 °C), exothermic DTA and DTG peaks (304 and 452 °C), weight loss 67.57% at 140 °C and 96.77% at 500°C).

Table 3
The results of thermal analysis of the thyme

	Water evolved			Thermal decomposition			Combustion of char		
	DTA T_{max} (°C)	DTG T_{max} (°C)	WLdes 140 °C (%)	DTA T_{max} (°C)	DTG T_{max} (°C)	EXO/DM (%)	DTA T_{max} (°C)	DTG T_{max} (°C)	WL 500 °C (%)
Newly gathered sample 2 (10 tests on the whole plant)									
Mean	85.2	85.4	64.9	305.9	305.9	70.3	454.4	454.4	96.6
S.D.	2.28	2.36	2.76	1.70	1.70	1.85	4.73	4.73	0.21
R.S.D.%	2.67	2.76	4.26	0.56	0.56	2.63	1.04	1.04	0.22
Newly gathered sample 7 (mean of three tests on each aerial part)									
Leaves	87.9	87.2	68.5	303.6	303.6	67.2	446.8	446.8	95.6
Stalks	79.7	79.1	58.3	303.0	294.3	60.7	440.0	440.0	96.7
Flowers	88.8	88.8	70.6	289.9	289.9	50.6	444.2	440.4	95.9
Dried powdered sample 2 (mean of three tests on each sample)									
Raw				298.9	283.5	68.4	433.8	433.8	97.3
Without Ext				297.4	278.7	72.5	430.7	430.7	91.7

T_{max}, temperature of peak maximum; WLdes, weight loss dessication; Ext, extractives; WL, weight loss; S.D., standard deviation; R.S.D., relative standard deviation.

loss (EXO/DM, %) corresponds to the centesimal ratio of weight losses (in the interval of the DTG peak with a maximum at about 300 °C) and the total dry matter volatilised.

The relative standard deviation was between 0.56 and 1.04% for the T_{max}, except for water evolving, the R.S.D. value was higher because the samples were not gathered and analysed in the same day. A high level of biopolymers in leaves can explain a high EXO/DM (67.2%). A DTG decreased T_{max} (corresponding to the thermal decomposition) and an increased EXO/DM (volatilisation loss) favour the fire risk.

Some variations, in temperature (°C) and in weight losses (%), were shown in the comparison of newly gathered samples 2 and 7 and dried powdered sample 2. The level of EXO/DM (70.3%), in newly gathered sample 2, was higher than that of each aerial part of sample 7. This may be due to higher cellulose level found in sample 2 (28.7%/DM) compared to sample 7 (20.8%/DM). In addition, we think that the physical state (freshly cut sample or dried powder) may play a role in the thermal behaviour of samples.

The essential oil coming from the 19 different samples was determined by gas chromatography (unpublished results). The oil showed two endothermic peaks by DTA: one at about 125 °C, due to *p*-cymene (bp = 177 °C) and γ-terpinene (bp = 183 °C) and another one at about 170 °C, corresponding to thymol (bp = 233 °C) and carvacrol (bp = 237 °C). The oil, with a majority of low boiling point components (such a *p*-cymene and γ-terpinene) will present an increasing fire risk compared to an oil with a majority of high boiling point components (thymol and carvacrol). The freshly cut sample did not show these endothermic DTA peaks, because of the low level of oil (about 2 ml/100 g dry matter) and the lack of sensitivity of the used method.

3.2.2. The comparison of thermal behaviour of thyme and other plants

The aim of this section is to compare the decomposition rate of several Mediterranean plants. In a previous publication [20], the values of EXO/DM were found to be 64.4 and 67.9% for rosemary and kermes leaves, respectively. The EXO/DM value for the thyme whole plant was 70.3%, which is mainly due to the presence of more volatiles, that may lead to increase the risk of fire.

Table 4
Thermal degradation and cellulose content in four Mediterranean plants

Samples	DTG peak (%/min)	EXO/DM (%/DM)	Cellulose (%/DM)
Mimosa			
Leaves	1.28	64.4	12.9
Branches	1.46	67.4	21.8
Kermes oak			
Leaves	1.56	67.9	17.9
Branches	1.89	72.2	24.9
Rosemary			
Leaves	1.22	64.4	15.3
Branches	2.00	73.9	39.2
Thyme			
Leaves (L)	1.30	70.3	23.4
Branches (B)	1.97	74.9	32.8
Mixture (L + B)	1.37	71.4	28.0

Mean of three different samples; DTG, derivative thermogravimetry; EXO/DM, volatilisation loss corresponding to the centesimal ratio of weight losses (in the interval of the DTG peak with a maximum at about 300 °C) and the total dry matter.

Previously [21], we found that cellulose produces maximum flammable volatiles at about 300°C which increase the risk of fire.

Four plants are compared in Table 4: mimosa (*Acacia dealbata*), kermes oak (*Quercus coccifera*), rosemary (*Rosmarinus officinalis*) and thyme (*Thymus vulgaris*). The decomposition rate (DTG, %/min) was correlated with the cellulose content in dried powdered samples [18].

It is well known, in Provence, that the Labiate family plants (such as rosemary and thyme) are responsible for the start of numerous forest fires. In addition, essential oil and cellulose (39.2% in rosemary branches and 32.8% in thyme branches) could explain the increasing risk of fire. In contrast, mimosa, which contains 13% of cellulose in leaves and no essential oil, has never been the cause of fire.

In Table 5, we present the thermal analysis results of the biopolymers (cellulose, holocellulose and lignin) obtained from thyme and argeras (*Ulex parviflorus*). Argeras is a well known in Provence as a flammable plant in summer, during the dry period. Table 5 shows the near values for cellulose obtained from thyme and argeras. Discrepancies in holocellulose (cellulose + hemicellulose) and lignin could be attributed to their

Table 5
The results of thermal analysis of biopolymers obtained from thyme and argeras

Biopolymers		Thermal decomposition				Combustion of char	
		DTA_{max} (°C)	DTG_{max} (°C)	DTG_{max} (%/min)	EXO/DM (%/DM)	DTA_{max} (°C)	DTG_{max} (°C)
Thyme (mean computed from three tests)							
Cellulose		301.4	291.3	7.54	73.3	449.0	449.0
Holocellulose		280.6	274.0	4.24	66.1	364.3	364.3
Lignin		298.4	299.7	5.49	53.5	451.2	451.2
Argeras (12 tests on each biopolymer)							
Cellulose	Mean	303.5	292.0	5.57	77.5	450.8	450.8
Holocellulose	Mean	293.3	283.1	2.82	70.8	392.0	392.0
Lignin	Mean	302.5	298.3	1.71	51.6	436.7	436.7

DTA, differential thermal analysis; DTG, derivative thermogravimetry; EXO/DM, volatilisation loss corresponding to the centesimal ratio of weight losses (in the interval of the DTG peak with a maximum at about 300 °C) and the total dry matter.

chemical structures; the decomposition rates of thyme components are higher than those of argeras.

3.2.3. *Kinetics of biopolymer decomposition*

Cellulose is a linear polymer of molecular weight higher than 100,000 and composed of D-glucose units ($C_6H_{10}O_5$) bounded together by ether bounds. Cellulose changes to levoglucosan and then to oxygenated products (C_1–C_4), such as, alcohols, carbonyls, acids and phenols [6–14].

The cellulose kinetic decomposition, observed previously, was first order [22–25]. The activation energy (E_a) of thyme's cellulose was determined, following a previously reported procedure [26]. In thermogravimetry, the two methods of either Flynn or Kissinger can be used [1].

In the Flynn's method, using the selected values of conversion, the temperature T (K) at the conversion level is measured for each thermal curve obtained for different heating rates. A plot of the logarithm of heating rate (β) versus the corresponding reciprocal temperature at constant conversion, is constructed. The plotted data should produce a straight line:

$$E_a = -R\frac{d\log\beta}{d(1/T)} \quad \text{where } R \text{ is perfect gas constant}$$

Kissinger supposed that the maximum of the reaction rate complies, practically, with the differential scanning calorimetry (DSC) or derivative thermogravimetry (DTG) maximum peak. In an earlier study [17], the near values (performed on eight samples) were, mean (R.S.D.%): 180.8 (1.80%) and 183.8 kJ mol^{-1} (2.84%) for Flynn's and Kissinger's methods, respectively.

Under air flow, E_a of cellulose was 184.7 kJ mol^{-1} (mean of five different samples of thyme) versus 183.8 kJ mol^{-1}, observed previously, for several plants [26].

Holocellulose is a mixture of cellulose and hemicellulose. Hemicelluloses are branched polymers of molecular weight higher than 30,000 and containing 50–200 units, mainly of D-xylose ($C_5H_{10}O_5$) and D-mannose ($C_6H_{12}O_6$). These pentosans and hexosans are the most abundant hemicelluloses [12].

The decomposition of holocellulose is also first order. For holocellulose, and under the same conditions that of cellulose, E_a was 195.6 kJ mole^{-1} (150–200 kJ mole^{-1} found, previously, for holocellulose obtained from five different species, [27]). These variations could be attributed to the chemical structure differences of hemicellulose. Notwithstanding the extensive literature pertaining to the pyrolysis of cellulose, fundamental studies on hemicellulose seem to be relatively rare. The hemicellulose containing, mainly, pentosan and hexosan groups [28,29], decompose to its monomer D-xylose or D-mannose, and furfural, furan, aldehyde and acetic acid.

It was earlier shown that the decomposition kinetics for lignin is different from the first-order kinetics observed for cellulose and holocellulose [26,30]. Lignin is a tridimensional polymer, which fixes together cellulose fiber, with phenylpropane units. It corresponds to a great number of aromatic cycles linked by furan rings or by ether bounds.

Lignin is obtained from leaves and flowers. We found a correlation between the maximum decomposition rate ($Y = \mathrm{DTG}$, %/min) and the heating rate (X, °C/min). This correlation exhibits a straight line in the interval 5–50 °C min^{-1}. We obtained the following equation for thyme:

$$Y = 0.189\mathrm{X} + 3.978$$

with $r = 0.998$ and 10 tests from 5 to 50°C min^{-1}

In a previous work [26], we observed a greater slope, for thorns and branches of *Ulex parviflorus*: 0.224; and a lower one for black pine cones of *Pinus halepensis*: 0.116. So, thyme's lignin present a higher decomposition rate that those of pine cone's lignin.

The lignins have very complex structures, for instance, the statistical model of Pine Kraft lignin consists of 14 aromatic rings with numerous substituents [31]. The lignin decomposes in the first stage by ether bond breaking, resulting in substituted phenols (cresols, syringaldehyde, and vanillin . . .). Upon increasing temperature (the second stage) the methoxy groups of the lignin and its aromatic derivatives go to methanol. Charcoal is also observed [12].

Our results show the increasing of lignin decomposition rate, expressed by the slope of this straight line. The flammability risk increases with the rate of mass loss and the evolved gases.

4. Conclusions

The fire risk is high for thyme, especially in dry periods. A great level of organic extractives, essential oil and biopolymers favour the flammability risk. Cellulose decomposes from 200 °C, with a maximum at about 300 °C, with flammable volatiles. The activation energy of cellulose is the same for every species. The fire risk increases, mainly due, to the presence of organic matter, such as, cellulose, hemicellulose and organic extractives. We observed, for the plant samples, a characteristic DTA exothermic peak and a DTG peak with a maximum at about 300 °C for all species. By thermal analysis, the reactivity is primarily indicated by the DTG peak temperature (lower temperature is equivalent to higher reactivity). So we could differentiate these species according to their decomposition, thanks to the amplitude of the DTG peak at about 300 °C.

Thermal analysis (TG, DTG, DTA) can provide a useful technique in the prevention of the forest fires.

Acknowledgements

We wish to thank F. Mambrini and P. Battestini for their technical collaboration and Meteo France for offering the precipitation values.

References

[1] J. Kaloustian, A.M. Pauli, J. Pastor, J. Appl. Polym. Sci. 83 (2002) 747.

[2] J. Kaloustian, A.M. Pauli, J. Pastor, J. Appl. Polym. Sci. 77 (2000) 1629.

[3] E. Leoni, P. Tomi, J. Kaloustian, N. Balbi, 32èmes Journées de Calorimétrie et d'Analyse Thermique, Hammamet, Tunisia, 2001.

[4] E. Leoni, P. Tomi, N. Balbi, A.F. Bernardini, 31èmes Journées de Calorimétrie et d'Analyse Thermique, Rouen, France, 2000.

[5] S. Fourment, J. Kaloustian, A.M. Pauli, J. Pastor, 31èmes Journées de Calorimétrie et d'Analyse Thermique, Rouen, France, 2000.

[6] S.B. Martin, R.W. Ramstad, Anal. Chem. 33 (1961) 982.

[7] R.F. Schwenker, L.R. Beck, J. Polym. Sci., Part C 2 (1963) 331.

[8] F.J. Kilzer, A. Broido, Pyrodynamics 2 (1965) 151.

[9] S. Glassner, A.R. Pierce, Anal. Chem. 37 (1965) 525.

[10] D. Dollimore, J.M. Hoath, Thermochim. Acta 45 (1981) 87.

[11] D. Dollimore, J.M. Hoath, Thermochim. Acta 45 (1981) 103.

[12] D. Masson, X. Deglise, Journées d'études ADITEC 82, Valorisation des sous-produits et des déchets des industries agro-alimentaires et agricoles, Lyon, France, 1982.

[13] D. Davies, A.R. Horrocks, Thermochim. Acta 63 (1983) 351.

[14] C. Devallencourt, J.M. Saiter, D. Capitaine, Polym. Degrad. Stability 52 (1996) 327.

[15] R.C. Pettersen, The chemical composition of wood, in: R.M. Rowell (Ed.), The Chemistry of Solid Wood: Advances in Chemistry, Series 207, American Chemical Society, Washington, DC, 1984 (Chapter 2).

[16] TAPPI (US Technical Association of Pulp and Paper Industry), Acid-Insoluble Lignin in Wood and Paper, norm T222, OS-74, 1974.

[17] J. Kaloustian, A.M. Pauli, J. Pastor, Acta Bot. Gallica 146 (1999) 311.

[18] J. Kaloustian, A.M. Pauli, J. Pastor, J. Therm. Anal. 50 (1997) 795.

[19] J. Kaloustian, A.M. Pauli, J. Pastor, J. Therm. Anal. 46 (1996) 1349.

[20] J. Kaloustian, A.M. Pauli, J. Pastor, J. Therm. Anal. 53 (1998) 57.

[21] J. Kaloustian, A.M. Pauli, J. Pastor, J. Therm. Anal. 46 (1996) 91.

[22] S.S. Alves, J.L. Figueiredo, J. Anal. Appl. Pyrolysis 15 (1989) 347.

[23] S.S. Alves, J.L. Figueiredo, J. Anal. Appl. Pyrolysis 17 (1989) 373.

[24] G. Varhegyi, M.J. Antal, P. Szabo, E. Jakab, F. Till, J. Therm. Anal. 47 (1996) 535.

[25] S. Cooley, M.J. Antal, J. Anal. Appl. Pyrolysis 14 (1988) 149.

[26] J. Kaloustian, A.M. Pauli, J. Pastor, J. Therm. Anal. Calorim. 61 (2000) 13.

[27] J. Kaloustian, A.M. Pauli, J. Pastor, J. Therm. Anal. Calorim. 63 (2001) 7.

[28] M. Rinaudo, Rev. F. Corps. Gras. 22 (1975) 429.

[29] N. Shukry, B.S. Girgis, M.Z. Sefain, Bull. Soc. Chim. F. 127 (1990) 515.

[30] J. Kaloustian, A.M. Pauli, J. Pastor, Acta Bot. Gallica 145 (1998) 307.

[31] R.A. Fenner, J.O. Lephardt, J. Agric. Food Chem. 29 (1981) 846.