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TG–FTIR analysis applied to the study of thermal behaviour of some edible mushrooms

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Abstract The article is devoted to the study on the thermal behaviour of three species of edible mushrooms: *Boletus edulis* (foot and cap), *Pleurotus ostreatus* (foot and cap), *Lactarius deterrimus* (cap) by the TG–FTIR-coupled technique, in air, over the 30–900 °C temperature range. The analysis of the TG–DTG–DTA curves reveals the thermal degradation mechanism to be complex and specific to every species under the recording conditions applied. A similar degradation mechanism is noticed for the foot and cap of *Pleurotus ostreatus* in comparison with the *Boletus edulis* and *Lactarius deterrimus* species where the mechanisms are different. The TG–FTIR analysis, combustion heats and IR spectra of the starting samples also support these results. The initial degradation temperatures from TG–DTG indicate the temperature range where these species are thermally stable and their nutrient features maintained making them proper for food. The TG–FTIR analysis gives information on the gaseous species evolved by the thermal degradation bringing thus a contribution to the elucidation of the changes developing by processing the edible mushrooms (industrialization, conservation, culinary preparations, etc.) at temperatures above the initial degradation temperature. At the same time, the environmental impact, when the mushroom failed cultures are burned, is also important.

Keywords Edible mushrooms · TG–FTIR analysis · Thermal stability

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Introduction

The chemical composition of the edible mushrooms is different from one species to another depending also on the growing stage, the nutrient substratum, the part submitted to analysis (cap, foot, lamella, etc.) and also on the clime conditions: the growing period, their age (if they are young or old) [1]. More than 200 macromycetes types, which grow spontaneously, include edible species proper for the food products. Some of them are known in the countryside for their medicinal properties [2, 3]. The thermal behaviour of the edible mushroom species is not yet to be found in the scientific literature.

Since these mushrooms are used for food either as such or thermally processed in industry (conservation, culinary preparations, etc.) and since the failed cultures might be capitalized by burning, this study is completely justified.

By taking into account the fact that the coupled TG–FTIR analysis has lately been proved to be very efficient in completing the thermal analysis data [4–9], we applied it for the first time in the present paper to study the thermal behaviour of the following edible mushroom species: *Boletus edulis* (**1**); (**1a**—foot; **1b**—cap); *Pleurotus ostreatus* **2** (**2a**—foot; **2b**—cap); and *Lactarius deterrimus* (**3**—cap).

Thus, the TG–DTG–DTA curves are indicative of a complex thermal degradation mechanism which is specific to each species under study [10–14]. A similar degradation

mechanism is noticed with the **2a** and **2b** *Pleurotus ostreatus* species compared to the **1a** and **1b** *Boletus edulis* and with the **3** *Lactarius deterrimus* species showing different degradation mechanisms. This conclusion is also supported by the TG–FTIR analysis where the FTIR spectra recorded at the same temperature (time) are identical for the **2a** and **2b**, *Pleurotus ostreatus* species (foot and cap) and different for the **1a** and **1b**, *Boletus edulis* and **3**, *Lactarius deterrimus* species.

The result is also confirmed by the FTIR spectra of the starting samples and by the combustion heats affording the conclusion that compositions of the **2a** and **2b** of the *Pleurotus* species (sample 2) are similar, while for the *Boletus edulis* **1a** and **1b** and *Lactarius deterrimus* **3** species they are different.

The initial degradation temperatures from TG–DTG indicate the temperature range where these species are thermally stable and proper for food consumption as such.

It can be noticed that the nitrogen-containing compounds suffer a thermo-oxidative degradation between 44.46 and 388.52 °C while between 388.52 and 643.8 °C, CO_2 and H_2O are formed from the carbohydrate compounds. The remaining residue could mainly consist of metal oxides coming from the minerals in the mushroom species under study.

Based on the above considerations, the article could bring valuable contributions to the elucidation of the modifications during the mushroom processing exceeding a certain temperature and also of the environmental impact of the gaseous species evolved when the failed cultures are burned.

Experimental

Materials

The mushroom species *Boletus edulis* (**1**), *Pleurotus ostreatus* (**2**) and si *Lactarius deterrimus* (**3**) were collected in September 2008 in the forest ecosystems located at 47 06′ N; 25 13′ E and altitude of 1600–1800 m in the National Park of Calimani (Romania). The mushrooms were separated from the earth remains and plant residues (leaves, roots, etc.) being then carried in paper bags and preserved at 4 °C for 24 h. The mushroom samples were dried in laboratory in Petri plates at the room temperature.

Boletus edulis is a common edible ectomycorrhizae species, found from August to October in deciduous and coniferous forests from mountainous regions. This species contains about 89% water, 2.7% proteins and 0.4% lipids along with great contents of E, D, K and B vitamins, oligoelements (selenium, kalium, iron) phosphorous, etc. [2].

Pleurotus ostreatus is an edible, saprophytic, facultative parasitic mushroom, which grows in large groups, imbricate, on deciduous wood, especially on beech. This species can be cultivated industrially.

The fruit body shows high contents of proteins (2.7–4%), carbohydrates (3.5–5%) and mineral salts (0.1–1.0%). The kalium, phosphorus, silicon, selenium contents, the lack of starch and sodium, and the low lipid content make this species proper for being consumed by diabetics and also for controlling the anaemia, the tiredness conditions and for the mineralizing effect.

The polysaccharides in fruit body and mycelium contain β-glucan, with antioxidant, anti-cholesterol, anti-viral and antibacterial effects, regulating the blood pressure and acting also as a nervous tonic and a cardiovascular protector. [3].

Lactarius deterrimus is an ectomycorrhizae species on spruce (*Picea abies*), found from July to September in coniferous forests from mountainous regions. It is recommended to be consumed well done. It contains proteins (2.5%), carbohydrates (2.8%), lipids (0.7%) and minerals (0.6%). [2].

Methods

TG–FTIR

TG–FTIR analyser consists of a TG/DTA Diamond (Perkin Elmer) thermo-balance and FTIR spectrophotometer (Spectrum 100) (Perkin Elmer), provided with a TG–FTIR (Perkin Elmer) gas transfer accessory and a FTIR gas cell of 100-mm length and KBr windows heated at 150 °C. The FTIR spectra were recorded within the 4000–700 cm^{-1} range at a resolution of 4 cm^{-1} and scanning rate of 200 cm/s, a single spectrum being recorded every 15 s by means of the Spectrum Time Base Perkin Elmer program. A G7 gas analyser (Dominic Hunter) supplies the dry air (pearl point: −50 °C) entering the TG/DTA analyser at a flow rate of 100 mL/min as well as the nitrogen for purging the analysis room of the FTIR spectrophotometer. The analysis was run with 8–10 mg sample placed into a platinum crucible, at a heating rate of 10 K/min within the 30–900 °C temperature range.

The gaseous species produced by the thermal degradation of the sample were identified by means of the standard IR spectra.

The FTIR spectra of the initial sample were recorded within 4000–400 cm^{-1}, in KBr pellet, using a Jasco FTIR 660 Plus device.

Berthelot calorimeter

The formation enthalpies of the sample were estimated from the combustion enthalpies [16] using a Berthelot calorimeter

(caloric bomb), the VEB (AB) Apparatus bau Postdam-Bahelsherg (Germany) model. The temperature variation during the sample combustion was measured using a Bekman thermometer of a 0.01 °C precision. The calorimeter standardization was made by the combustion of a known amount of benzoic acid $\left(\Delta_c H^0_{298} = 3.2257 \times 10^6 \mathrm{J/mol}\right)$.

Results and discussion

The TG–DTG–DTA curves indicate that the thermal degradation mechanism under the recording conditions is complex and specific to every species (Fig. 1). The degradation mechanism of the species **2** is similar for **2a** (foot) and **2b** (cap) whose thermograms are identical and different from the samples **1a** and **1b** (foot and cap, respectively) and the sample **3**, (cap).

The samples **1a** and **1b** are decomposed into five and six stages, respectively. The samples **2a** and **2b** show four degradation stages as also does the sample **3**.

The characteristic amounts from the TG–DTG curves are presented in Table 1.

As made evident by data in Table 1, the stage 0 developing between 50 and 138 °C corresponds to the elimination of physically retained water although the samples were previously dried. The water amount varies between 1.5 and 4.5% and the higher the water amount, the wider the elimination temperature range is. The real thermal degradation begins in the stage 1.

By comparing the characteristic amounts in Table 1 for the sample **2** (**2a** and **2b**) which is decomposed into three stages, it can be noticed that the temperature ranges of degradation, ΔT°C which are of 356,65 (**2a**) and 356,62 (**2b**), the temperatures at the maximum degradation rate, T_m, the mass losses in every stage as well as the resulting residue (%) are the same within the limits of experimental values.

These findings would suggest similar chemical compositions of the foot (**2a**) and cap (**2b**) of this species.

The thermal degradations of the samples **1a** and **1b** proceed into four and five stages, respectively. The temperature range (ΔT) where the degradation takes place at 554.23 °C (**1a**) and 495.55 °C (**1b**) as well as the characteristic temperatures, the mass losses in every stage (%) and the resulting residue (%) are different which means that the chemical compositions of the foot (**1a**) and of the cap (**1b**) are different.

The sample **3** is decomposed into three stages similar to the species of the sample **2**. The characteristic temperatures and the mass losses in every stage (%) are close to those of the species in sample **2**; on the other hand, the residue amount higher than the sum of the residues of the samples **1a** and **1b**, and **2a** and **2b**, respectively, would suggest a higher mineral content of the sample **3** than the samples **1** and **2**.

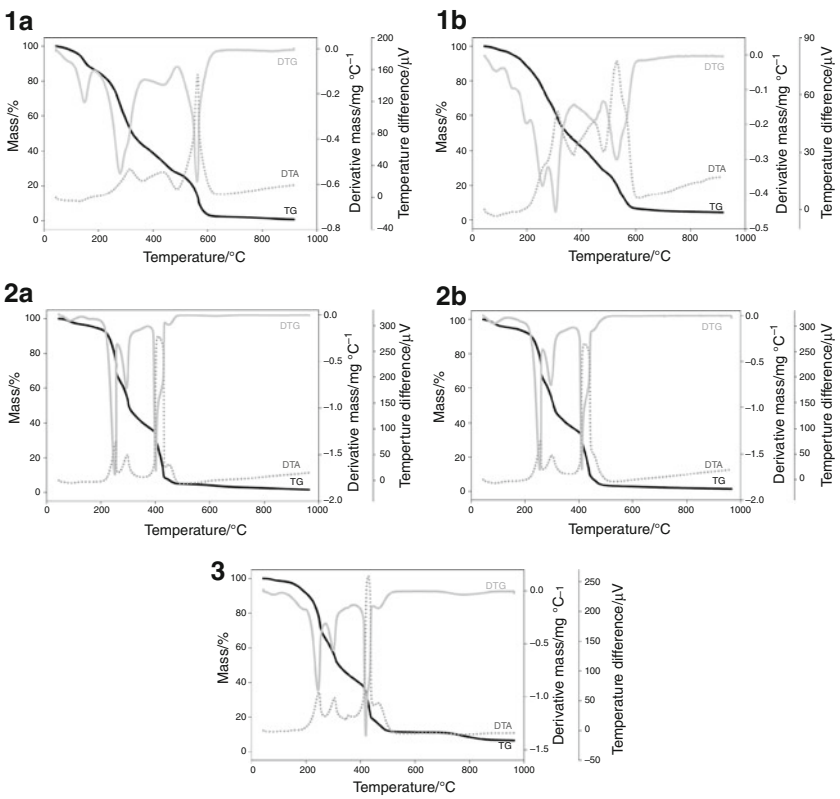

Fig. 1 The TG–DTG–DTA curves for macromycetes **1a**, **1b**, **2a**, **2b** and **3**

Table 1 Characteristic temperatures from TG–DTG and mass losses in every stage

Thermal method	Temperature range	Stage	Characteristic temperature	Sample				
				1a	**1b**	**2a**	**2b**	**3**
TG–DTG	30–900 °C	0	T_i/°C	49.15	47.33	49.40	44.46	48.17
			T_m/°C	–	90.37	90.90	90.28	89.53
			T_f/°C	89.57	119.50	138.08	134.38	115.75
			W_α/%	1.43	2.83	3.46	4.65	1.68
		I	T_i/°C	89.57	119.50	138.05	134.38	115.75
			T_{inf}/°C	–	156.60	194.12	202.63	204.45
			T_m/°C	152.27	203.94	252.11	255.64	245.84
			T_f/°C	190.79	216.50	265.80	270.23	276.39
			W_α/%	12.57	11.43	30.99	29.798	34.24
		II	T_i/°C	190.79	216.50	265.80	29.798	276.39
			T_m/°C	281.50	259.13	295.93	270.23	302.80
			T_f/°C	373.82	281.68	375.81	297.18	380.81
			W_α/%	43.90	20.11	27.98	29.63	22.74
		III	T_i/°C	373.82	281.68	375.81	388.52	380.81
			T_m/°C	444.00	306.92	435.92	443.86	447.72
			T_f/°C	494.8	376.76	494.70	515.64	535.00
			W_α/%	15.15	34.40	36.62	33.04	29.87
		IV	T_i/°C	494.8	376.76			
			T_m/°C	571.10	446.70			
			T_f/°C	643.80	484.25			
			W_α/%	24.80	2.91			
		V	T_i/°C		484.25			
			T_m/°C		530.83			
			T_f/°C		615.05			
			W_α/%		22.04			
			Residue/%	2.45	6.30	4.95	3.20	11.47

T_i initial degradation temperature, T_{inf} temperature corresponding to the DTG curve inflexion, T_m temperature at the maximum degradation rate, W mass loss (%)

The initial thermal degradation temperatures from TG–DTG (Table 1) indicate the following series of the thermal stabilities:

$$\mathbf{2a} \geq \mathbf{2b} > \mathbf{1b} > \mathbf{3} > \mathbf{1a}$$

because T_i are

$$\begin{aligned} T_{i2a} = 138.05\,^\circ\mathrm{C} &\geq T_{i2b} \\ = 134.38\,^\circ\mathrm{C} &> T_{i1b} > 119.5\,^\circ\mathrm{C} > T_{i3} \\ = 115.75\,^\circ\mathrm{C} &> T_{i1a} = 89.57\,^\circ\mathrm{C} \end{aligned}$$

which also confirms the above conclusions.

The characteristic temperatures at the maximum of the DTA curves for the thermo-oxidative degradation stages of the samples are given in Table 2.

It is noticed that the temperatures at the maximum of the DTA process in all the stages are close for the species of the sample **2** ($T_{m2a} \sim T_{m2b}$) and different for the species of the sample **1** ($T_{m1a} \neq T_{m1b}$), while with the species of the sample **3** the value T_{m3} is closer to T_{m2b} in all degradation stages which confirms the above conclusions.

The combustion heats [15, 16] of the samples in Table 3 support the results obtained from TG–DTG–DTA (Fig. 1).

The combustion heats of the samples **2a** and **2b** are close and different from those of the samples, **1a**, **1b** and **3**. The values of the combustion heats are somehow lower than for the wood (16800–20100 J/g) [16] which affords the conclusion that these species might be used also as a fuel as the wood is.

The TG–FTIR analysis derive from recording the spectra of the gaseous species produced by the thermal degradation in air of the species under study as a function of temperature (time) is in agreement with the conclusions drawn from TG–DTG–DTA and combustion heats, Fig. 2.

Table 2 Characteristic temperatures from DTA

Thermal method	Temperature range	Stage	Characteristic temperature	Sample					Nature of the process
				1a	**1b**	**2a**	**2b**	**3**	
DTA	30–900 °C	0	T_m/°C	99.00	89.22	94.07	92.25	82.90	Endo
		I	T_m/°C	135.73	–	256.00	260.08	249.15	Exo
		II	T_m/°C	319.66	269.60	299.38	303.43	307.06	Exo
		III	T_m/°C	438.63	314.45	450.28	460.39	461.72	Exo
		IV	T_m/°C	572.96	447.39	–	–	–	Exo
		V	T_m/°C	–	530.65	–	–	–	Exo
			T_f	635.10	611.94	530.36	536.88	536.88	

T_m temperature at the DTA maximum, T_f final temperature of thermal degradation from DTA

Table 3 Heats of combustion

Sample	*m*/*g*	Δ*T*/°C	$-\Delta H_C$/J g^{-1}
1a	0.747	1.21	$17.4255 \cdot 10^3$
1b	0.949	1.45	$16.4647 \cdot 10^3$
2a	0.500	0.80	$17.2427 \cdot 10^3$
2b	0.700	1.11	$17.0547 \cdot 10^3$
3	0.177	0.28	$17.0242 \cdot 10^3$

m/*g* sample mass, Δ*T* temperature variation during combustion

In this connection, the FTIR spectra in Fig. 3 recorded with the **2a** and **2b** samples at the same degradation temperature (time), 221–224 °C, are identical unlike the TG–FTIR spectra at the same temperature (time) of the samples **1a** and **1b** which are entirely different.

The TG–FTIR analysis of the gaseous species produced by the thermal degradation in air using standard IR spectra [17, 18] made evident the following:

1a: H_2O, CO_2, CO;
1b: H_2O, CO_2, CO, NH_3, N_2O;
2a: H_2O, CO_2, CO, CH_4, NH_3;
2b: H_2O, CO_2, CO, CH_4, NH_3;
3a: H_2O, CO_2, CO, NH_3, CH_4, N_2O;

The study reveals the fact that within the 138–350 °C the nitrogen-containing compounds in the mushroom species are degraded, and then the thermo-oxidative degradation of the carbohydrates affords the formation of CO_2 and H_2O; the remaining residue consists of the metal oxides coming from the metals contained.

The 3D-FTIR correlations between the gas amounts produced by thermal degradation of the samples in air revealed higher amounts of CO_2 in comparison with the other gaseous species. For illustrated, the 3D-FTIR spectra of the sample **3** are depicted in Fig. 4.

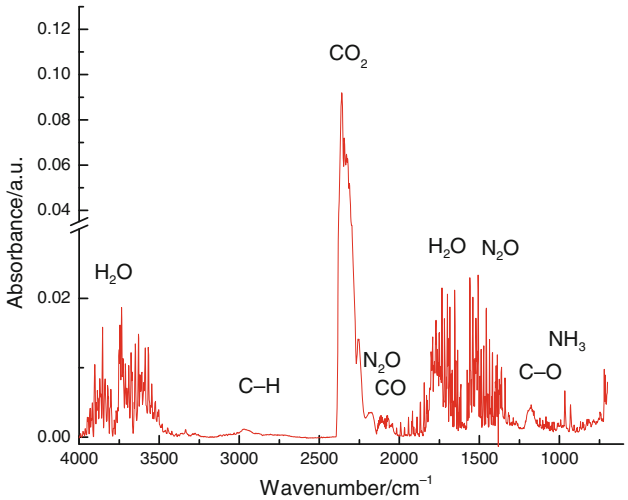

Fig. 2 FT IR spectra of resulting gases by the thermal degradation of sample **2** at 286 °C

The results obtained from the TG–FTIR analysis data and combustion heats are in good agreement and attest the conclusions coming from TG, DTG and DTA.

This study ascertains the temperature range within which the mushrooms species in the samples under study are thermally stable. The temperatures where the modifications in the chemical composition and hence in their nutritive features begin are also made evident.

It is also noticed that the thermal effect caused by burning these mushroom species is similar to that of wood burning which would suggest the possibility of using the failed mushroom cultures as a fuel. The identification of the gaseous species eliminated under the influence of temperature is an important contribution brought to the elucidation of their environmental impact.

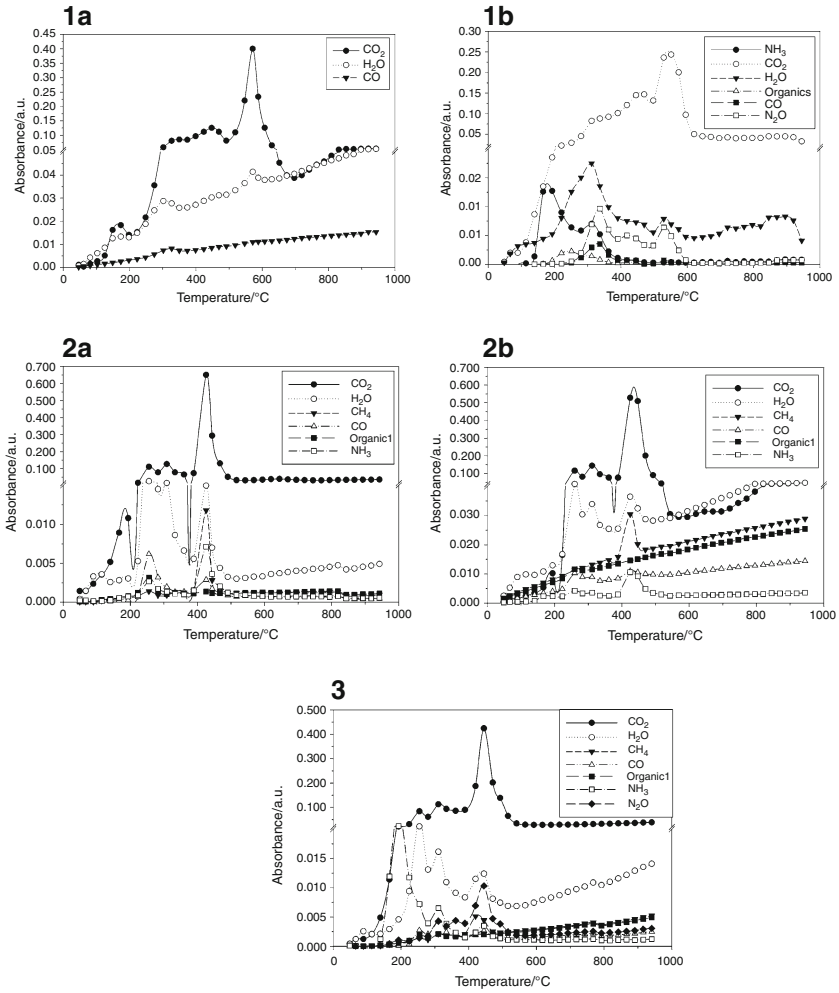

Fig. 3 FT IR spectra of the gaseous species resulting from samples **1a**, **1b**, **2a**, **2b** and **3**

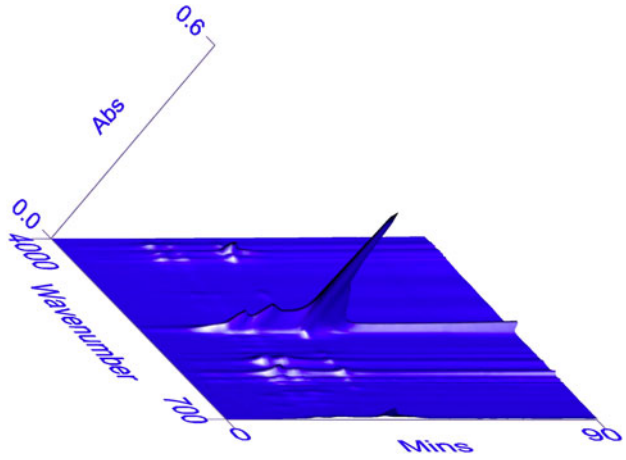

Fig. 4 3D-FT IR spectra obtained for the thermal degradation of the sample **3**

Conclusions

– As evidenced by the TG–DTG–DTA analysis, the thermal degradation mechanism in air of the mushroom species under study is complex and specific, being at the same time similar for the samples **2a** and **2b** of the species **2**.

– Since the degradation temperature range, ΔT, the temperatures at the maximum degradation rate, the mass losses in every stage (%), the amount of the resulting residue as well as the temperatures at the maximum of the DTA process are the same, it follows that the chemical compositions of the foot and cap of the sample **2** are identical. For the other species, these amounts are different.

– The initial degradation temperatures (Table 1) are indicative of the following series of the thermal stabilities of the samples:

$$\mathbf{2a} \geq \mathbf{2b} > \mathbf{1b} > \mathbf{3} > \mathbf{1a}$$

– The values of the combustion heats of the samples are in agreement with the conclusions drawn from TG–DTG–DTA being also close to the combustion heat of wood.

- The TG–FTIR analysis by means of the spectra of the gaseous species evolved by thermal degradation in air in function of temperature (time) agrees with the conclusions from TG–DTG–DTA. The FTIR spectra of the samples **2a** and **2b** at the same temperature (time) are identical, while for the samples **1a** and **1b** and **3** they are different.
- The results of the TG–FTIR analysis are in good agreement with those from the combustion heats and support the conclusions from TG–DTG–DTA.
- The study ascertains the temperature range where these species are thermally stable, the temperatures where modifications in their composition begin causing some changes in their nutritive characteristics. The possible environmental impact of the gaseous species evolved by thermal degradation is also important.

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