



Antioxidant effect of dehydrated rosemary leaves in ripened semi-hard cheese: A study using coupled TG–DSC–FTIR (EGA)



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ABSTRACT

The Evolved Gas Analysis (EGA) is a group of techniques (in this case coupled TG–DSC and FTIR) that can provide information regarding mass changes, exothermal and endothermal events, as well as gaseous products that are evolved during events. In this study, semi-hard cheeses were manufactured and the lipid fractions were assessed by the above-mentioned techniques and others such GC/MS and ¹H NMR, and kinetic parameters were calculated using thermogravimetry. The samples were divided into three portions: (a) cheeses 24 h after manufacture; (b) cheeses after 60 days of ripening; (c) cheeses covered with lard and rosemary after 60 days of ripening. It was observed that the fat from samples treated with rosemary leaves showed higher decomposition temperatures (TG), higher resistance to the oxidation process ($T_p = 310.2\text{ }^\circ\text{C}$) and enthalpy (1228.5 J g^{-1}). The FTIR spectroscopy of the gaseous products of decomposition obtained simultaneously with TG–DSC curves revealed that the main bands could be attributed to –C–H, –COOH stretching with the formation of CO, CO₂ and tetradecanoic acid-7-oxo-methylester compounds. An increase in the value of the activation energy in cheese covered with rosemary leaves was associated with antioxidant activity.

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1. Introduction

Lipids (oils and fats) are unstable substances and they may exhibit auto-oxidation, which is an irreversible process leading to rancidity and a reduction in flavour and nutritive value. The lipid oxidation is the major cause of deterioration during the shelf-life of foods (Basaga, Tekkaya, & Acikel, 1987; Casarotti & Jorge, 2014; Georgantelis, Blekas, Katikou, Ambrosiadis, & Fletouris, 2007).

In order to retard, reduce and/or prevent oxidative deterioration in foods, as well as the alterations of sensory properties of foods some antioxidants can be added. The main synthetic substances used for these purposes are: butylated hydroxy anisole (BHA), butylated hydroxy toluene (BHT), propyl-galate (PG) and tert-butyl hydroxyl quinone (TBHQ) (Frutos & Hernández-Herrero, 2005; Kulisik, Radonic, Katalinik, & Milos, 2004). However, the literature reports that these substances have been suspected of causing or promoting negative health effects (Karpinska, Borowski, &

Danowski-Oziewicz, 2001; Kulisik et al., 2004; Peiretti, Gai, Ortoffi, Aigotti, & Medana, 2012) and consequently, consumers have shown a growing tendency to reject many synthetic additives in foods, which are mainly synthetic antioxidants (Gamel & Kiritsakis, 1999).

The antioxidant capacity of rosemary spice (as oil, extracts or leaves) is associated with the presence of phenolic compounds, such as carnosic acid, rosmarinic acid, carnosol, rosmanol, rosmariquinone and rosmaridiphenol, which react with the free radicals formed during the oxidation process (Aruoma, Halliwell, Aeschbach, & Löliger, 1992) and break the chain reaction by donating electrons (Georgantelis et al., 2007).

The main properties described in the literature and attributed to rosemary spice as oil, an extract, or even the leaves are: antibacterial (Dragoni & Vallone, 2009), antifungal (Dragoni & Vallone, 2009; Rasooli et al., 2008), antimicrobial (Moreira, Ponce, Del Valle, & Roura, 2005; Ponce, Roura, & Moreira, 2011), bio-preservative (Ponce et al., 2011), insecticide (Dragoni & Vallone, 2009), metal chelating additive (Basaga et al., 1987) and antioxidant (Basaga et al., 1987; Casarotti & Jorge, 2014; Martínez, Penci,

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Ixatina, Ribotta, & Maestri, 2013; Moreira et al., 2005; Olmedo, Nepote, & Grosso, 2013; Peiretti et al., 2012).

Thus, the aim of this study was to investigate the thermal behaviour of samples from the lipid fraction obtained from semi-hard cheeses made with raw milk covered (and not covered) with lard and rosemary leaves. This investigation was carried out to assess the antioxidative effect of rosemary leaves under the following conditions: (a) fat from uncoated cheese extracted 24 h (one day) after manufacture, (b) fat from uncoated cheese extracted 1440 h (60 days) after manufacture and (c) fat from cheese covered with lard and rosemary leaves and extracted 1440 h (60 days) after manufacture.

The GC/MS and ^1H NMR techniques were used for determination of fatty acids composition and structural modifications of fats. The thermal analysis (TG, DSC, EGA) were performed to determine the gases produced during thermal decomposition and made kinetic studies, for evaluate the antioxidant activity of rosemary.

2. Materials and methods

Samples were taken from two batches of cheese produced at the dairy pilot plant at the Technological School of Milk and Cheese of Campos Gerais (ETLQueijos-UEPG) at the State University of Ponta Grossa (UEPG), Paraná, Brazil. The protocol consisted of the use of 75 L (each batch) of raw milk from Holstein cows. The manufacturing process started with the addition of commercial lyophilised direct-to-vat thermophilic starter culture (Biolact T-12) containing *Streptococcus thermophilus*, *Lactobacillus helveticus*, *Lactobacillus delbrueckii* spp. *bulgaricus* and *Lactobacillus casei*. Twenty min after the inoculation of the culture, 0.4 mL L $^{-1}$ of a solution at 5×10^2 g L $^{-1}$ of calcium chloride and 0.016 g L $^{-1}$ rennet powder (HA-LA 2154 IMCU, Chr. Hansen) were added. After coagulation, the curd was cut with the aid of curd cutters into 1 cm edged cubes, followed by continuous and slow stirring of the mass for 20 min. This was followed by partial syneresis (removing 0.3 L L $^{-1}$ of the whey), a second agitation and the addition of 0.2 L L $^{-1}$ water at 70–80 °C. After 60 min the mass was pre-compressed (twice the weight of the mass) for 15 min, transferred to polypropylene moulds (110 mm diameter by 86 mm height), and subjected to pressing with the same mass weight for 90 min and turning every 30 min. When the pressing time was reached, the cheeses were removed from the moulds, placed in brine at 160 g L $^{-1}$ for 24 h. Subsequently, the samples were taken to the maturation chamber with a controlled temperature of 12 ± 2 °C and a relative humidity of 85–90%. From each batch 16 pieces of cheese of about 400 g were obtained.

On the fifteenth day of maturation (ripening), half the cheeses were covered with a layer of lard in a proportion of 30 g kg $^{-1}$ and dehydrated rosemary leaves at a ratio of 40 g kg $^{-1}$ and were maintained for 45 more days, (i.e., 60 days of ripening). The uncoated cheeses were also ripened for 60 days.

One piece of cheese from each batch was removed from the maturation chamber for the extraction of fat on each of the designated dates - 24 h of ripening (one day), which was called sample (a); after 1440 h (60 days) of ripening, the uncoated cheeses, which were called sample (b); and after 1440 h (60 days) of ripening, the cheeses covered with 30 g kg $^{-1}$ lard and 40 g kg $^{-1}$ rosemary leaves, which were called sample (c). The cheeses coated with rosemary were scraped to remove the rosemary and fat before analysis.

The procedure for fat extraction was in accordance with that described by Taracki, Temiz, Aykut, and Turhan (2011) and was as follows: up to 10 g of ground sample was added to 60 mL of chloroform:ethanol (2:1 mL:mL), which was stirred using an Ultra Turrax homogeniser for 3 min. Then 15 mL of 1×10^{-3} Mol L $^{-1}$

solution of calcium chloride was added, followed by vigorous stirring for 30 s. The mixture was centrifuged ($2000 \times g$) for around 15 min. The phases were then separated and evaporated to chloroform phase in a rotary evaporator under reduced pressure at 40 °C.

2.1. Thermogravimetry and differential scanning calorimetry (TG–DSC)

The simultaneous TG–DSC curves were obtained by using a Mettler Toledo TGA–DSC 1star^e system. The purge gas was an air flow of 50 mL min $^{-1}$ and a heating rate of 10 °C min $^{-1}$ was adopted, with samples weighing about 20 mg. Alumina crucibles were used to record the TG–DSC curves. The DSC curves permitted the determination of the thermal events, such as exotherm or endotherm reactions, as well as making it possible to determine the main oxidation temperatures and to calculate the enthalpy (ΔH).

2.2. Evolved gas analysis (EGA)

The measurements of the gaseous products were carried by using a Nicolet FT-IR spectrophotometer with gas cell and DTGS KBr detector coupled to a Mettler Toledo TG–DSC. The furnace and the heated gas cell (250 °C) were coupled through a heated (225 °C) 120 cm stainless steel line transfer with diameter of 3 mm, both purged with dry air (50 mL min $^{-1}$). The FTIR spectra were recorded with 16 scans per spectrum at a resolution of 4 cm $^{-1}$. The FTIR spectra of the decomposition gases were analysed using the OMNIC ThermoScientific v. 8.0 software programme.

2.3. Differential scanning calorimetry (DSC)

The Differential Scanning Calorimetry (DSC) curves were obtained using DSC-Q200 (TA Instruments, USA) equipment. The instrument was previously calibrated using Indium 99.99% purity, $m.p. = 156.6$ °C, $\Delta H = 28.56$ J g $^{-1}$. The samples were heated from 30 °C to 600 °C using an aluminum crucible with a pierced lid with a 1.0 mm diameter orifice and approximately 4 mg of each sample under an air flow rate of 150 mL min $^{-1}$ at a heating rate of 10 °C min $^{-1}$.

2.4. GC/MS analysis

The triacylglycerol (fat cheese) samples were initially submitted to a transesterification procedure in order to convert the triacylglycerol into fatty acid methyl esters. The determinations of fatty acid composition by GC/MS were performed on a Varian Saturn 2000R instrument equipped with an Agilent DB-225-MS capillary column. The GC conditions were as follows: initial temperature, 50 °C; final temperature, 210 °C; heating rate, 40 °C min $^{-1}$. Carrier gas, helium, at the flow rate of 1.0 mL min $^{-1}$.

In order to make it possible to determine the fatty acid composition by means of GC analysis, initially the retention times were determined by injecting a standard solution containing a mixture of fatty acid methyl esters.

2.5. Kinetic study

The kinetic study of the oxidation process was based on Ozawa's non-isothermal method and was applied to the thermogravimetric (TG) curves. The results obtained using the thermal analysis system TGA-50 (Shimadzu, Japan) were under the following conditions: 4 mg of sample were used in an open alumina crucible in an air flow of 150 mL min $^{-1}$; the samples were heated from 30 °C to 600 °C at heating rates of 10, 15, 20, 25 and 30 °C min $^{-1}$. The instrument was

first calibrated with standard weight and calcium oxalate monohydrate. ^1H NMR.

The NMR analyzes were performed on a Bruker 400 NMR spectrometer operating a 9.4 T observing the ^1H nuclei at 400.13 MHz. For this, aliquots of approximately 10 μl of each sample were directly transferred into 5-mm NMR tubes and the volume was completed to 500 μl with CDCl_3 containing $5 \times 10^{-3} \text{ g L}^{-1}$ TMS. The ^1H NMR spectra were recorded at 30 $^\circ\text{C}$. by accumulating thirty two scans, a relaxation delay of 1 s, spectral width of ~ 9.1 ppm and 64 K data points. The ^1H NMR chemical shifts are expressed in ppm related to the TMS signal at 0.00 ppm as internal reference.

3. Results and discussion

The TG–DSC curves of the fat from the cheeses (Fig. 1) showed three steps of mass loss. It is suggested that the first step was associated with the loss of low residual solvent used in the extraction of the samples, which in the DSC curves was observed as a large endotherm phenomenon, with mass loss of 3.92, 2.73 and 1.21% of initial mass. The second step was due to the decomposition of monounsaturated and polyunsaturated fatty acids, and the third step was due to the decomposition of saturated fatty acids, which in the DSC curves were observed as two exothermic peaks.

The main values related to the simultaneous TG–DSC curves are gathered together in Table 1: The DSC curves are depicted in Fig. 2 and showed similar behaviour to the TG–DSC curves. There were

Table 1

Main results obtained for each step of TG–DSC curves: (a) 24 h of ripening; (b) uncoated – 1440 h of ripening; (c) coated – 1440 h of ripening.

Samples		1st Step	2nd Step	3rd Step	Ash
(a)	θ ($^\circ\text{C}$)	30–199	199–414	414–585	–
	T_p ($^\circ\text{C}$)	–	355 exo	490exo	–
	Δm (%)	3.92	83.39	12.50	0.19
(b)	θ ($^\circ\text{C}$)	30–200	200–420	420–584	–
	T_p ($^\circ\text{C}$)	–	356exo	488exo; 520exo	–
	Δm (%)	2.73	84.90	12.27	0.10
(c)	θ ($^\circ\text{C}$)	30–220	220–422	422–595	–
	T_p ($^\circ\text{C}$)	–	356exo	490exo; 555exo	–
	Δm (%)	1.21	85.36	13.30	0.13

θ = temperature range; T_p = peak temperature; Δm = mass loss.

two major exothermic peaks for all the samples; the first peak with T_p at 299, 305 and 319 $^\circ\text{C}$, respectively, and the second with T_p at 512, 511 and 511 $^\circ\text{C}$, respectively.

The curves followed the model of the autocatalytic reaction of lipids by free radicals. Initially, peroxide formation occurred and the second peak resulted from the decomposition of peroxides into secondary oxidation products (Ixtaina, Nolasco, & Tomás, 2012).

In agreement with the literature (Polavka, Paligová, Cvengros, & Simon, 2005), the polymerisation of monomers formed during the decomposition of polyunsaturated fatty acids was an endothermic step and the oxidative decomposition of unsaturated and saturated fatty acids referred to an exothermic event.

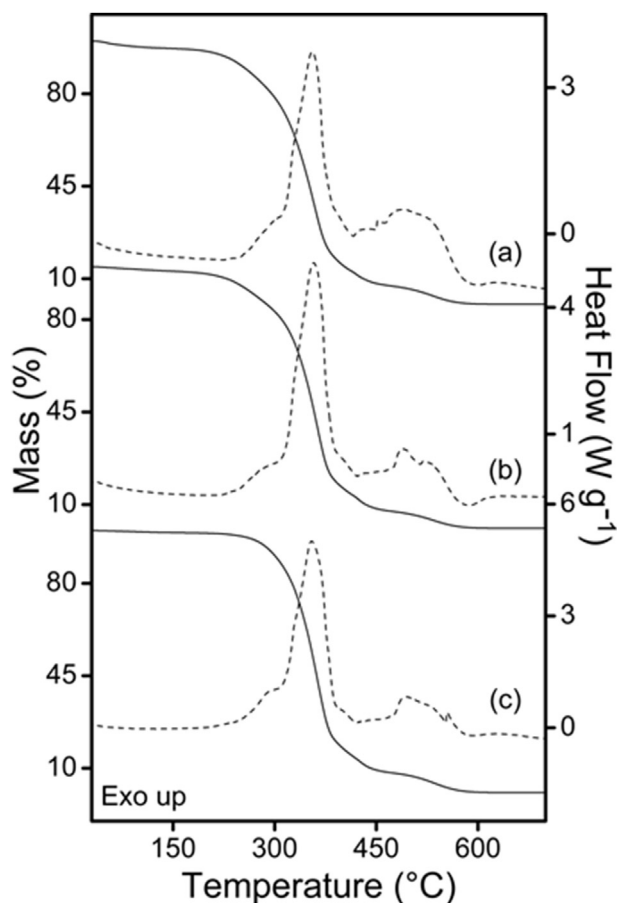


Fig. 1. Simultaneous TG–DSC curves of fat extracted from semi-hard cheese: (a) fat from uncoated cheese extracted after 24 h (one day) of manufacture, (b) fat from uncoated cheese extracted after 1440 h (60 days) of ripening and (c) fat from cheese covered with lard and rosemary leaves extracted after 1440 h (60 days) of ripening. TG – solid line, DSC – dash line.

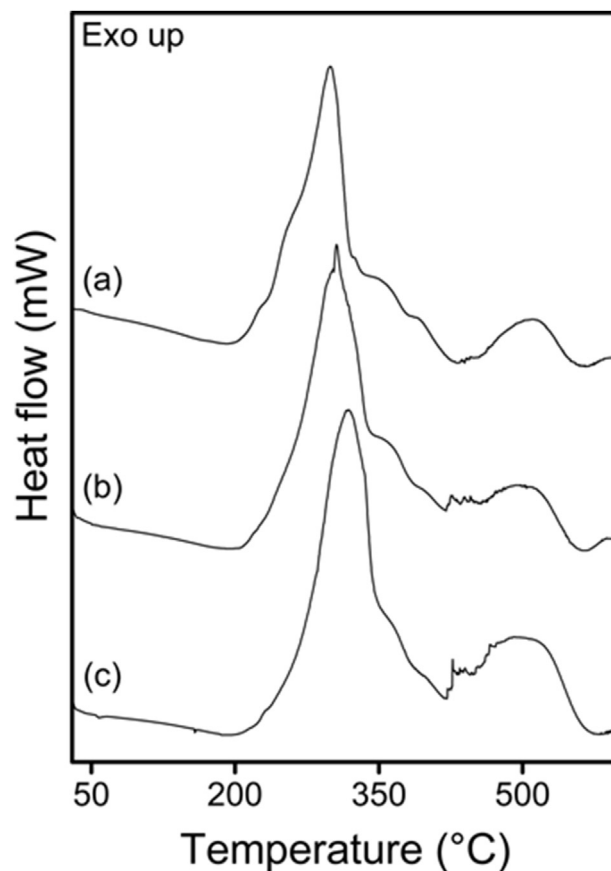
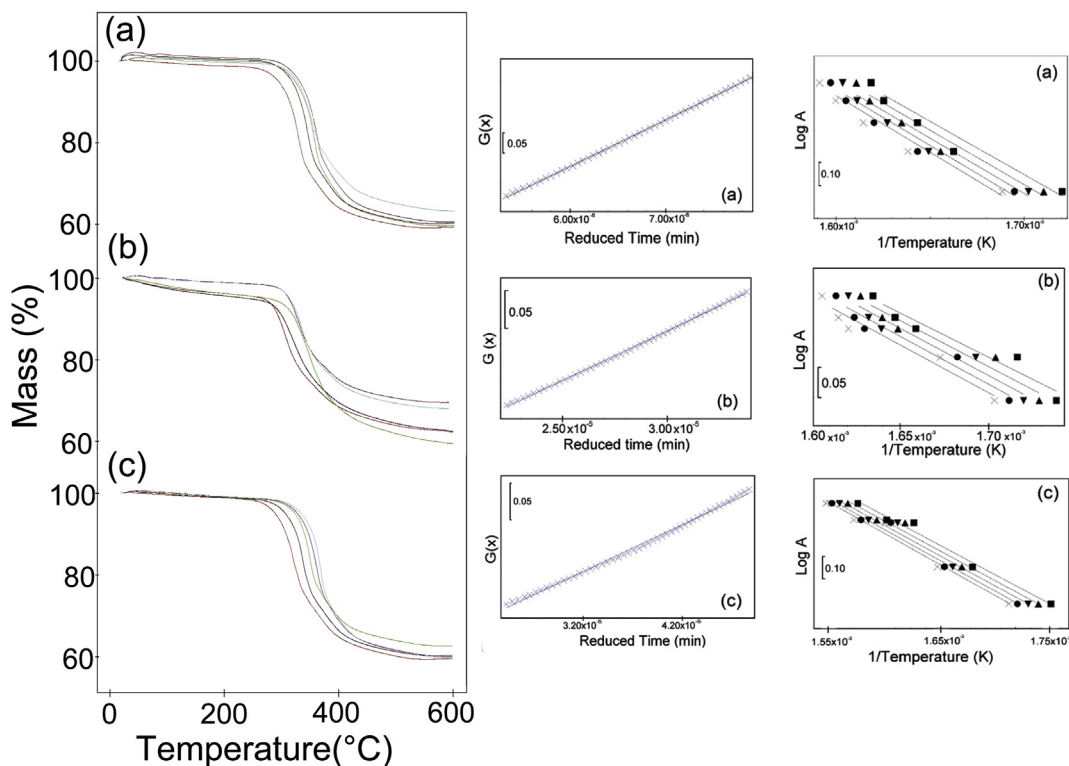


Fig. 2. DSC curves of fat extracted from semi-hard cheese: (a) fat from uncoated cheese extracted after 24 h (one day) of manufacture, (b) fat from uncoated cheese extracted after 1440 h (60 days) of ripening and (c) fat from cheese covered with lard and rosemary leaves extracted after 1440 h (60 days) of ripening.

Table 2

Results of DSC analysis: (a) 24 h of ripening; (b) uncoated – 1440 h of ripening; (c) coated – 1440 h of ripening.

Samples	1st Peak				2nd Peak			
	T _o (°C)	T _p (°C)	T _c (°C)	ΔH (J g ⁻¹)	T _o (°C)	T _p (°C)	T _c (°C)	ΔH (J g ⁻¹)
(a)	250.84 ± 0.51 ^b	304.50 ± 0.71 ^b	320.63 ± 4.76 ^a	1149.00 ± 48.10 ^b	—	—	—	—
(b)	251.20 ± 0.44 ^b	301.07 ± 1.55 ^c	331.08 ± 6.47 ^a	1161.50 ± 38.90 ^b	439.80 ± 23.70 ^a	512.56 ± 10.08 ^a	552.99 ± 5.36 ^a	305.90
(c)	269.32 ± 0.22 ^a	310.20 ± 1.40 ^d	322.56 ± 9.61 ^a	1228.50 ± 19.10 ^a	424.64 ± 9.10 ^a	509.29 ± 2.35 ^a	547.86 ± 16.33 ^a	450.40

“T_o” Onset temperature, “T_p” Peak temperature, “T_c” Conclusion temperature, “ΔH” Enthalpy.^{abc} Different letters in the same column indicate significant statistical differences between cheeses (Tukey Test, p < 0.05).**Fig. 3.** Kinetic values obtained from TG curves of fat extracted from semi-hard cheese: (a) fat from uncoated cheese extracted after 24 h (one day) of manufacture, (b) fat from uncoated cheese extracted after 1440 h (60 days) of ripening and (c) fat from cheese covered with lard and rosemary leaves extracted after 1440 h (60 days) of ripening.

The GC/MS results (supplementary materials) showed that fat cheeses contained predominantly monounsaturated and saturated fatty acids. No endothermic events were observed in the DSC curves obtained in this study. Szabo, Chambre, and Iditoui (2012) observed the same trend in swine fat.

The results obtained from the DSC curves are shown in Table 2. The onset temperature (T_o), peak temperature (T_p) and endset or conclusion temperature (T_c), as well as enthalpy, were calculated.

Many factors influence the activation energy required to promote enthalpic events, such as the presence of antioxidants and the relationship between saturated and unsaturated fatty acids (Simon, Kolman, Niklova, & Schmidt, 2000).

The thermal decomposition of unsaturated fatty acids requires less energy than the decomposition of saturated fatty acids (Kasprzycha-Guttman & Cozeniak, 1991). Using the study of the oxidation kinetics (Fig. 3) it was possible to determine the activation energy of the event by calculating the first 10% of mass loss associated with the oxidation of the samples.

According to Kowalski, Ratusz, Miciula, and Krygier (1997), the thermal oxidation of lipids is an exothermic reaction that can be measured by enthalpy variations. In the present study the fat extracted from the cheese covered with rosemary leaves showed

higher oxidation temperatures (T_o and T_p) as well as higher enthalpy values (ΔH). The ¹H RMN results (supplementary materials) show that no structural modifications, suggesting that the antioxidant activity occurs due rosemary presence, demonstrated when the fat is subjected to thermal stress.

The antioxidant activity of rosemary is attributed to the presence of phenolic diterpenes, such as carnosol and carnosic acid, as well as its capacity to donate electrons to free radicals and terminate the chain reaction (Madsen & Bertelsen, 1995).

The results obtained from the kinetic study of the oxidation of the samples using the Flynn-Wall-Ozawa non-isothermal method are shown in Table 3.

Table 3

Kinetic parameters obtained of oxidation: (a) 24 h of ripening; (b) uncoated – 1440 h of ripening; (c) coated – 1440 h of ripening.

Samples	E _a (kJ mol ⁻¹)	Reaction order	Arrhenius frequency factor
(a)	56.15 ± 1.73	1st	1.30 × 10 ⁻⁴
(b)	59.05 ± 1.48	1st	6.34 × 10 ⁻⁴
(c)	85.91 ± 2.07	1st	3.88 × 10 ⁻⁶

E_a = activation energy.

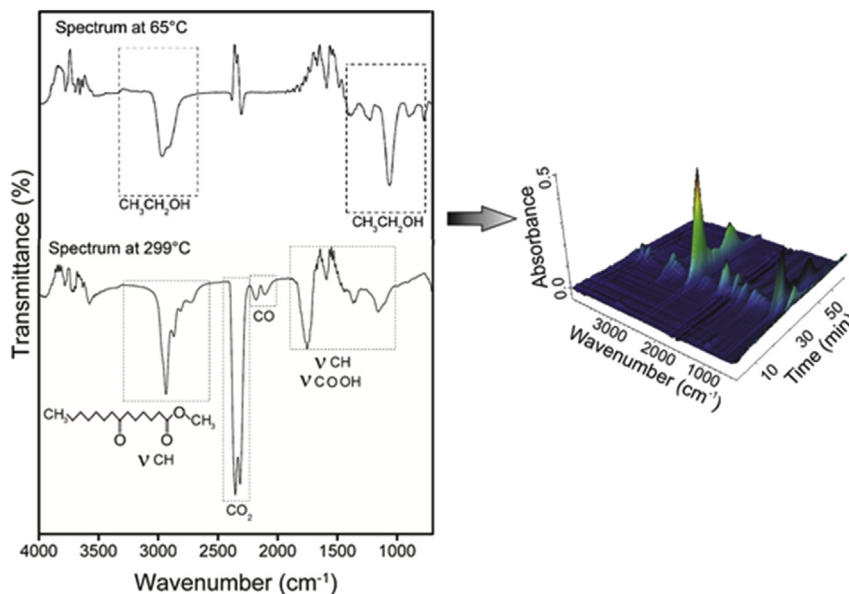


Fig. 4. FTIR spectrum (left) of the gaseous products from the thermal decomposition of semi-hard cheese at 65 °C and at 299 °C and 3D spectrum (right). All samples showed the same products of thermal decomposition.

The results regarding activation energy, in agreement with this method (Flynn-Wall-Ozawa), were in accordance with the enthalpy values, namely that sample (c) showed higher E_a and ΔH oxidation values, suggesting that the cheeses covered with rosemary had a higher resistance to the oxidation process. The FTIR spectrum of the decomposition gases are given in Fig. 4.

With regards to the FTIR spectrum, all the studied samples showed similar behaviour. This technique suggests by comparing experimental spectrum and those of the library in OMNIC from “Thermo Fischer Scientific Inc., USA, Software OMNIC 8.0.342.” software, which the release of ethanol in the first stage of decomposition and in a second stage was observed the release from a mixture of gases that have bands that can be assigned to $-C-H$, $-COOH$ stretching in agreement with literature (Silverstein, Bassler, & Morrill, 2005) as well as compounds $C_{15}H_{28}O_3$ (Tetradecanoic acid-7-oxo-methylester), as well as the main bands from CO and CO_2 .

4. Conclusion

In this study the samples covered with rosemary leaves showed an increase in the stability of the lipid fraction when compared with early maturation cheeses or uncoated cheeses. The lipid fraction of the coated cheeses showed greater stability, with higher degradation and oxidation temperatures when the thermo-oxidative process was accelerated. The sample containing rosemary had an average increase of 53% in the value of the activation energy associated with the oxidation of the samples.

FTIR showed the release of the gases in the first two steps, which were release residues of the solvent used in the extraction of the samples (CH_3CH_2OH), and in the second stage a gas mixture was observed more effectively from CO_2 and CO, which was attributed to CH and COOH stretching.

5. Conflict of interest statement

The authors declare that there are no conflicts of interest.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.lwt.2015.03.108>.

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