Biblid: 1821-4487 (2016) 20; 1; p 73-76
UDK: 637.524
Original Scientific Paper
Originalni naučni rad

THERMAL ANLYSIS AND LIPID OXIDATIVE STABILITY OF SERBIAN TRADITITIONAL DRY FERMENTED SAUSAGE FROM SREM COUNTY

TERMALNA ANALIZA I OKSIDATIVNA STABILNOST MASTI DOMAĆE FERMENTISANE SUŠENE SREMSKE KOBASICE

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ABSTRACT

Thermal characteristics of tradititional dry fermented sausage from Srem County was studied by Differential Scanning Calorimetry (DSC).

The aim of the study was to obtain the thermal characteristics and lipid oxidative stability of Serbian tradititional dry fermented sausage from Srem County and considering results obtained could gave information about the quality and durability of sausage.

The DSC thermogram of the sausage's meat assayed in this work, showed the characteristic endothermal transition in the low temperature range from -35 °C to -10 °C correspondning to water melting and in the temperature range from 90 °C to 120 °C correspondning to water evaporation.

The DSC thermogram of the fat from sausage has three endothermal transitions, specific for pork lard. Oxidation stability of fat from the sausage was checked by DSC-OOT method and the kinetic parameters of the lipid oxidation (E_a energy of activation, Z preexponential factor and k oxidation rate constant) were obtained by the Kissinger-Akahira-Sunose (KAS) method.

From DSC results obtained the free and bound water were determined, and information about lipid oxidation of sausage's fat suggested good overall stability and quality of meat product.

Key words: *fermented sausage, thermal analysis, oxidation stability.*

REZIME

Termalna svojstva tradicionalno osušene fermentisane domaće sremske kobasice praćena su metodom diferancijalne skenirajuće kalorimetrije (DSC).

Cilj ovog rada je bio da se utvrde termalna svojstva i oksidativne osobine, s obzirom na oksidativnu stabilnost masti, tradicionalno osušene fermentisane domaće sremske kobasice. Zahvaljući dobijenim rezultatima termalne analize, moguće je dobiti informacije o kvalitetu i trajnosti kobasice.

Iz DSC termograma dobijenih za meso kobasice moguće je razlikovti dva endotermna prelaza koji su karakteristični za meso i to niskotermperaturski prelaz u temperaturskom opsegu od -35°C do -10°C koji odgovara procesu topljenja leda I endotermalni prelaz na višim temperaturama, u temperaturskom opsegu od 90°C do 120°C, koji odgovara procesu isparavanja vode. Nisu nađeni termalni prelazi koji odgovaraju denaturaciji proteina.

Iz dobijenh DSC termograma uzorka koji predstavlja mast iz domaće sremske kobasice, mogu se videti tri, za mast karaktristična endotermna prlaza i to: niskotemperaturski prelaz u opsegu temperature od -2°C do 5°C, koji odgovara procesu topljenja leda i dva prelaza sa vrhom pika na temperaturama 28°C i 43°C, koji odgovaraju procesu topljenja masti.

Oksidativna stabilnost masti iz kobasice praćena je DSC -OOT metodom te su dobijeni kinetički parametri oksidacije lipida. Energija aktivaciije (E_a), prdeeksponencijalni faktor (Z) i konstanta brzine reakcije (k) dobijeni su Kissinger-Akahira-Sunose (KAS) metodom za određivanje kinetičkih parametara.

Ključne reči: *sremska kobasica, termalna analiza, oksidativna stabilnost.*

INTRODUCTION

Traditional dry fermented sausage has been produced for long time in the area of Srem County, Republic of Serbia. It is produced exclusively from pork meat and fat and spices.

Physico-chemical properties of foods are temperature-dependent, with a special sensitivity in the temperature range in which a phase change of water takes place. This temperature region depends on the composition of the food. The thermal characteristics of the food are highly dependent on the amount of the frozen water, as well as of the quantity of water which does not freeze, even at low temperatures *(Lind, 1991).*

The investigation of the freezing, melting point and amount of unfreezable water is useful for the modeling of food stability, and can give useful information regarding stability and quality of meat products *(Aktas et al., 1997; Roos 2003; Tolstorebrov et al., 2014)*. Dry fermented sausages are susceptible to lipid oxidation that can deteriorate their sensorial properties, by generation of compounds such as n-alkenals, dienals and aldehydes, which are associated with a rancid taste and odor *(Krkić et al., 2013)*. Lipid oxidation is responsible for chemical changes in fats and oils that lead to food spoilage and flavor deterioration. Oxidation can also affect the nutritional value of food by decomposition of vitamins and unsaturated essential fatty acids (*Ansorena & Astiasarán, 2004*). A good understanding of lipid oxidation kinetics can improve our abilities to formulate food products that maintain the existing quality in food system and minimize production of undesirable breakdown components. Kinetic data are essential for predicting oxidative stability of fats and oils under various heat processing, storage and distribution conditions. The transfer of an oxygen molecule to an unsaturated fatty acid requires energy. This process can easily be determined by differential scanning calorimetry (DSC). Among all various methods that measure the extent of lipid oxidation, DSC is widely used as an analytical, diagnostic and research tool from which relevant information,

such as onset temperature of oxidation (T_{on}), height, shape and position of peaks are obtained and used for subsequent kinetic calculations *(Thurgod et al., 2007; Tan 2001; Adhvary et al., 2000; Kamal-Eldin 2006; Sathive et al., 2008).*

The purpose of this work was to evaluate the thermal and lipid oxidative stability characteristics of Serbian tradititional dry fermented sausage from Srem County. The investigation of the freezing, melting point and amount of unfreezable water is useful for the modeling of sausage stability. Considering results obtained by thermal analysis, conclusions about the thermal and oxidative stability, which are crucial for quality and durability of sausage, has been reached.

MATERIAL AND METHOD

Pig, pork meat and sausages were produced into household in Ruma Pecinici, Srem, Serbia by a farmer Ranko Birac. The process of sausage making has been proceeded in the home made, traditional manner, in the one butch, about 20 kg of sausages have been produced in the end of process. Production procedure and traditional conditions during ripening has been as follows: pork meat (deboned pork neck, loin and shoulder) has been grounded and 2 % of NaCl had been added, hot peppers and garlic has been added by personal taste (about 0.2 %). The mixed sausage meat were stuffed and cased into natural casings. Sausages were then drained for one day, smoked for one day and finally drayed for 20-38 days into draft (15-18 °C). The samples of sausages used in this work, has been taken in the end of production process.

The samples (weight 5-8 mg) of mehanicaly defatted part of the sausage (meat) and the samples (weight 5-8 mg) of mehanicaly separated fat from the sausage were heated in the temperature range from -80 °C to 200 °C into hermeticaly siled Al pans in N_2 , with purge flow of 50 ml / min, using DSC Q1000 TA Instruments (Delaware USA). The pans were sealed with a T zero® DSC Sample Encapsulation Press (TA Instruments, USA). The samples were placed by an auto sampler into the DSC cell.

In the aim to obtain kinetic parameters of lipid oxidation fat samples (weight 3±0.3 mg) from sausage were heated at different heating rates (β) : 5, 10 , 15 and 20 °C/min, in temperature interval from 20 °C to 250 °C by DSC Oxidation onset temperature method (*ASTM 2009*). Samples were heated in open aluminum pans with an oxygen purge flow of 50ml/min, using DSC Q1000 TA Instruments (Delaware USA) method. The onset temperature T_o was determined from obtained DSC curves by TA Instruments Universal analysis 2000, Version 4.1.0.16 software. T_o was defined as the temperature at which the heat flow significantly deviates from the baseline, when rapid increase in the rate of oxidation is observed. This temperature is obtained from extrapolating the tangent drawn on the steepest slope of reaction exotherm. The first process at T_o is oxidation, and the seccond one at T_p, temperature maximum of first peak, could indicate the start of the fat thermal decomposition *(Thurgod et al., 2007).* Arrhenius rate constant *(k)*, activation energies *(E_a)* and preexponential factors *(Z)* were calculated according to the *Kissinger-Akahira-Sunose (KAS)* method (*Vyazovkin et al., 2011*). Assuming an overall first order process, the heat evolved (H) at time t is proportional to the amount of reacted substrate *(Thurgod et al., 2007).*

The amount of unfreezable water - free water was detected by the DSC melting curve analysis according to Quinn (*Quinn et al., 1988, Tolstorebrov et al., 2014).*

Chemical composition of sausages

Total protein content was 36 .1 %, fat 35.0 %, water content was 25.3 % and ash content was 1.2 %. The chemical composition was evaluated by determining of the moisture content (SRP ISO 1442, 1997), total protein (SRP ISO 937, 1992), fat (SRP ISO 1443, 1997), total ash (SRP ISO 936, 1998.

RESULTS AND DISCUSSION

Thermal characterization of sausage's meat, mehanicaly defatted part of the sausage, has been provided by DSC. The DSC heat flow curves obtained for sausage's meat showed the characteristic endotherm in the low temperature range from -35 °C to -10 °C corresponding to water melting and endotherm in the temperature range from 90 °C to 120 °C correspondingto water evaporation (Figure 1).

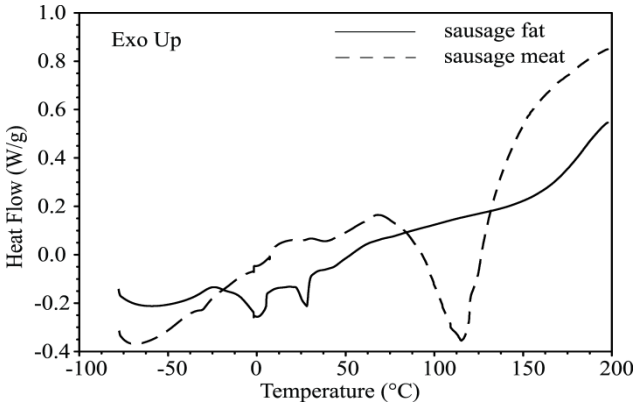


Fig. 1. The DSC curve of sausage's meat (mehanicaly defatted part of the sausage)(- -) and sausage's fat (—)

Free water has been obtained according to Quinn (*Quinn et al., 1988, Tolstorebrov et al., 2014).* The total and free water contents of the sample, initial (T_{o1}), maximum (T_m) and end (T_{end1}) temperatures and enthalpy of ice melting and water evaporation, as determined by DSC, are presented in *Table 1.*

The water contents of the meat samples were classified into two categories; free and bound water, based on a temperature of -40 °C *(Aktas et al., 1997; van der Sman and Boer, 2005)*. This is the reference temperature, accepted by numerous researchers (*Aktas et al., 1997; van der Sman and Boer, 2005)* where the water content that achieves complete freezing is termed as a free water and that remaining unfrozen is termed as bound water. Thermal transitions found in the our study correspond to defined processes of ice melting (T_{m1}) and water evaporation (T_{m2}) in the meat samples found in the literature (*Aktas et al., 1997; Roos* 2003; *Marchetti et a., 2013*). From results obtained it can be assumed that existence of the charactersistic thermal behavior for meat samples found for dry fermented sausage from Srem county provide information about free water in the sample,

Table 1. Thermodynamical pharameters and total and free water obtained from DSC curve for sample of meat from defatted sausage and fat from sausage

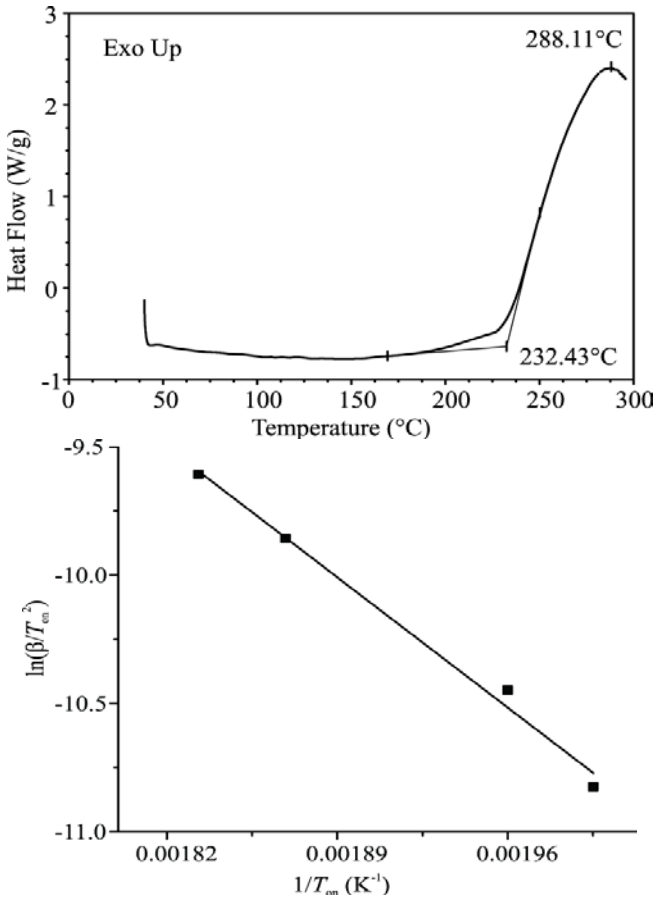
Samp.	T_{o1} (C°)	T_{m1} (C°)	T_{end1} (C°)	ΔH_1 (J/g)	T_{o2} (C°)	T_{m2} (C°)	T_{end2} (C°)	ΔH_2 (J/g)	T_{o3} (C°)	T_{m3} (C°)	T_{end3} (C°)	ΔH_3 (J/g)	Free water (g/g_{fw})	Moist. (%)
Meat	-35.0	-30.3	-26.6	1.16	82.6	115	157	347.4	-	-	-	-	0.005	25.3
Fat	-2.3	-1.7	5.6	19.52	21.3	28.1	29.9	9.49	35.3	43.6	59.7	2.62	0.06	

which is important for durability, shelf life and texture characteristics of sample. Obtained results for free water were lower than results for free water obtained for fresh meat *(van der Sman and Boer, 2005)* as it can be expected.

The DSC curve of the sausage's fat is presented on the Figure 1.

The DSC thermogram of the fat from sausage has three endothermal transitions, specific for pig lard in the nitrogen atmosphere (Figure 2. and Table 1.). First transition with peak minimum at -1.7 °C corresponds to water melting, second and third transitions with peak minim at 28.1 °C and on 43.6 °C, corresponds to fat melting (*Svenstrup et al., 2005*).

Kinetic parameters of lipid oxidation: Arrhenius rate constant (k), activation energies (E_a) and preexponential factors (Z) were calculated from result obtained from DSC-OOT curves, according to the *Kissinger-Akahira-Sunose (KAS)* method (*Vyazovkin et al., 2011*). Obtained parameters are presented on *Table 2* and in *Figure 2.*



Figu. 2. a) The typical DSC-OOT curve of sausage's fat; b) Plot of ln ß/T_{on}^2 versus inverse of onset temperature.

Table 2. Kinetical parameters of sausage's fat oxidation obtained from DSC-OOT curves

slope	intercept	Ea (kJ/mol)	Z (min^{-1})	$^{*}k_{25}$ (min^{-1})	$^{**}k_{120}$ (min^{-1})
7251.58	3.69739	60.29	292542.3	$8.0x10^{-6}$	$2.856 x10^{-4}$

*rate constant at 25 °C; **rate constant at 120 ° C.

Obtained kinetic parameters of fat oxidation are in agreement to the literature (*Saldaña and Martínez-Monteagudo, 2013).* As pork fat is mostly composed of triacylglyceroles with saturated and monosaturated fatty acids *(Petron et al., 2004)* values for kinetic parameters of fat oxidation (E_a and k) obtained in this work are also comparable to literautre data obtained for oxidation of saturated fatty acids palmitic (C16:0) and stearic (C18:0) and monosaturated oleic (C18:1) fatty acid *(Litwinienko and Kasprzycka-Guttman, 2000*; *Webb and O'Neill, 2008). From data obtained it could be proposed that sausage's* lipids were not in the stage of oxidation in which the secondary oxidation products were produced, which are the main reason of rancid taste.

CONCLUSION

From DSC results obtained, the free and bound water were determined. From the results obtained it can be assumed that existence of the charactersistic thermal behavior for meat samples found for dry fermented sausage from Srem county provide information about free water in the sample, which is important for durability, shelf life and texture characteristics of sample.

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ACKNOWLEDGMENT: This work was supported by the Ministry of Education and Science of the Republic of Serbia, under the Projects No TR-31055 and TR-31093.

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Received: 09. 03. 2016. Accepted: 06. 04. 2016.