KINETICS OF HYDROPEROXIDES FORMATION DURING HEAT TREATMENT OF MEAT EMULSIONS

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Background

The lipid oxidation is an extremely complex process what implies several reactions which give place to great variety of physical and chemical changes. The nature and extension of these changes are influenced by a great number of variables (light, air, temperature, pH, etc.). To explain the experimental results, has been postulated a simplified free radicals mechanism in three stages: initiation, propagation and termination.

Since evolution of the reaction [RH] + O_2 → free radicals, it is thermodynamically difficult, the production of the first necessary radicals to begin the propagation of the reaction is usually gotten by means of a catalyst. It has been proposed that initiation stage takes place for decomposition of hydroperoxide by means of a metallic catalyst or light exposure. Recently it has been postulated that it is the singulet oxigen the implied species, which acts making the pigments of the plants and animal tissues aware.

Once formed enough number of free radicals [R·], the chain reaction spreads when capturing atoms of hydrogen through double bounds. In these positions, after oxygen addition, are formed the peroxides radicals [ROO·] that in turn capture hydrogen of the metilenic groups [RH] of other molecules to give hidroperoxides [ROOH] and groups [R·]; these in turn react with the oxygen repeating the sequence of described reaction again.

The hydroperoxides, primary products of lipid oxidation, are relatively unstable, and they intervene in numerous and complex rupture reactions and interaction with compounds of different molecular weights, able to produce aromas, being also biologically significant.

Recently Adachi et al. (1995) revised the kinetics of the chemical reactions included in the development of the oxidative rancidity and informed that until then, to be the autooxidation a quite complex process that takes place through the initiation, propagation and termination stages, the kinetics must be analyzed in each stage in particular way.

Now, if the whole autooxidative process could express through a kinetic equation and if that equation, was only in function of the quantities of non-reacion substrate and oxygen, we could predict the autooxidative process for all conditions. This could allow to compare the suceptibility of several lipids to autooxidation.

According to the reaction mechanisms, the speed of lipid oxidation could be high when big quantities of free radicals are in the propagation stage. In the early states, the initiation and propagation reactions are the dominant ones, while in later states, due to the increment of the concentration of free radicals, the termination reactions begin to have importance. In the final states, the probability of occurrence of the initiation reactions and of propagation it is low due to the decrease of the concentration of substrates (fatty acids). (Özilgen, 1990)

Generally, kinetic models for oxidation were based on simple model systems or pure lipids and the adjusting differences to the same ones begin to appear when these models are extrapolated to complex meat systems, also is added the fact that at high temperatures the oxidative decomposition of meat systems is developed quickly, existing differences among high and low temperatures of oxidation (Henderson, 1980).

Objetive

The aim of this work was to study the hydroperoxides formation kinetics of meat emulsion systems during cooking at different temperatures.

Methods

Model system: 48% of beef, 35 % pork, 15 % lard and 2% NaCl were ground through 6 mm plates and emulsified in a colloidal mill. The meat emulsion prepared in colloidal mill, was mouldered in patties with the same weight (100 g), diameter (90 mm) and height (20 mm). They were divided into three batches (in duplicated) and cooked in a static system at 60, 80 and 100 °C, respectively. Lipid oxidation evolution was followed for 10 hs.

Determination of Lipid Oxidation: The lipidic fraction was extracted by Bligh and Dyer method (1959) using a mixture of Chloroform: Methanol:Water (33:42:24). The concentration of chloroformic layer was carried out in a Rotavapor BÜCHI (R 114), at 50 °C, under modified atmosphere.

Peroxide Value (PV): Lipidic fraction obtained was used for determining Peroxides Values. Determination of Peroxide Value was carried out using the AOCS iodometric method. Cd 8-5, using a solution of sodium thiosulfate 0,01 N. The results are expressed as miliequivalent of peroxide by kg of sample.

Determination of kinetic parameters: For the determination of kinetic parameters we proceeded according to the integral method of analysis of data, in which a particular kinetic equation is tested, integrated and calculated data of the concentration are compared in front of the time with experimental data. If fit is not satisfactory, it is suggested, and tested, another kinetic equation.

Results and Discussion

The Peroxide value increased in all samples for all temperatures and times (Table 1).

The classic molecular models of lipid oxidation establish that reactions happen through mechanisms in chain controlled by formation of free radicals with three typical steps: initiation, propagation and termination, being the initiation step the most important on kinetic.

On the base of described pattern of reaction, in the initiation step, mono and bi molecular reactions would be responables of oxidative changes through hidroperoxide decomposition.

At the beginning of initiation stage, low concentrations of peroxides favors a monomolecular reaction, but when concentration of peroxides reaches a critical value reaction pathway change to bimolecular (Ortolá, 1998).

According to these hypotheses the equations proposed for initiation stage are:

Monomolecular Reaction: $dPV/dt = k_1 . PV^{1/2}$

Bimolecular Reaction: $dPV/dt = k_2 / PV$

Where PV= Peroxide Value (meq Perox/kg sample).

k_1 and k_2 = specific reaction rate in Hs^{-1} $[PV]^{1/2}$ and Hs^{-1} $[PV]^2$, respectively.

t= time.

Fit of equations proposed to experimental data is shown in Figure 1 for all tested temperatures and for both reaction orders.

Inflection point, whose value agree with beginning of bimolecular reaction, was calculated by best adjusting value with maximum number of observed data. In samples cooked at 80 and 100 °C inflection point was reached at four hours of heating, in samples cooked at 60 °C this behavior was not observed, evidencing a best fit to monomolecular equation. This could be due to thermal treatment at lower temperature didn't generate enough number of necessary free radicals to begin bimolecular reaction stage.

The kinetic parameters, obtained from graphics, can be observed in table 2.

In this table is possible to observe that k values were affected by different heating temperatures, being bigger to higher cooking temperature. On the other hand, bimolecular reactions showed higher specific reaction rate for respective tested temperatures.

Utilizando la ecuación de Arrhenius se pudo determinar que la energía de activación involucrada en la reacción bimolecular fue de 21758,2 Cal y en la monomolecular 6529,8 Cal, lo cual nos estaría indicando que la etapa de reacción bimolecular es más sensible a los cambios de temperatura.

Conclusions

The proposed equations, which contemplate hydroperoxide formation through reactions mono- and bi- molecular, allowed to describe with a good fit the oxidative process in meat emulsions cooked at different temperatures.

References

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Table 1. Peroxide Values (meq Peroxide/Kg sample)

Time (h)	PV (60°C)	PV (80°C)	PV (100°C)
0	0.530 ± 0.064	0.429 ± 0.047	0.278 ± 0.014
2	0.237 ± 0.023	0.821 ± 0.023	0.762 ± 0.016
4	0.634 ± 0.018	1.080 ± 0.035	1.926 ± 0.050
6	0.644 ± 0.122	2.628 ± 0.206	1.670 ± 0.044
8	1.535 ± 0.065	3.091 ± 0.122	6.219 ± 0.262
10	1.706 ± 0.032	3.379 ± 0.109	7.720 ± 0.170

Table 2. Calculated kinetic parameters

Temperature	C_0	C_{max}	Monomolecular		Bimolecular	
			k_1	R^2	k_2	R^2
PV (100°C)	0.278	7.720	0.430	0.98	5.089	0.89
PV (80°C)	0.429	3.379	0.192	0.97	0.825	0.93
PV (60°C)	0.530	1.706	0.147	0.75	-	-

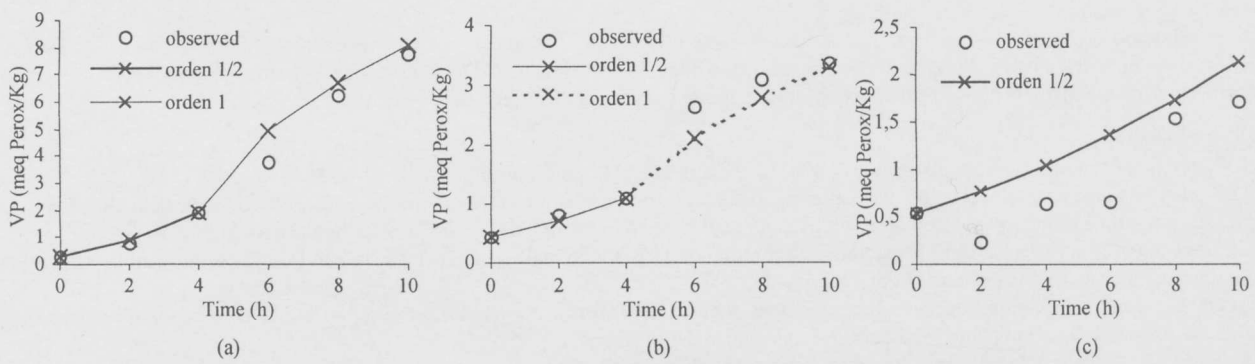

Fig 1. Evolution of Peroxide Values in meat emulsions cooked at different temperatures. a) 100 °C; b) 80 °C; c) 60°C .