MATHEMATICAL MODELING OF VITAMIN C LOSSES IN LEMONS DURING THERMAL TREATMENTS

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Abstract: Predicting the evolution of vitamin C concentration in different thermal treatments could be beneficial in offering an estimative nutritive value for food products which are in the conceptual stage. Known for its chemical instability, vitamin C can be deactivated by a wide range of oxidizing agents, but in food industry the most common cause of vitamin C reduction is the use of various thermal processes alongside raw materials conversion into the final products. Mathematical analysis for a comparative study about the variations of vitamin C concentrations in lemons, variations produced by the uses of low, medium and respectively high temperature treatments is presented in this paper.

Keywords: *vitamin C, food processing, mathematical analysis, lemons*

INTRODUCTION

Literature offers little or scattered information about the changes in concentrations of vitamin C in lemons due to different heat treatments conditions. The objective of this work is to check if experimental data collected in previous experiments [1] can be represented by a single mathematical model with and without the Arrhenius equation. This analysis may be used for better understanding the effects of heat processing and storage temperatures on vitamin C.
The lemons were chosen due to the high vitamin C content (50 mg/100 g product) and for their wide spread uses in human alimentation. Citrus fruits, tomatoes, strawberries, bell peppers and broccoli are good examples of foods rich in vitamin C [2].

MATERIALS AND METHODS

The experimental data were imported from a previous published paper [1]. A brief overview of experimental approaches is presented bellow.
For a better mimic of thermal conditions in food processing the experimental program was created to cover a wide range of temperature and time intervals (Table 1).

Table 1. *Experimental conditions for thermal treatments*

Apparatus	Temperature [°C]	Time interval
Dry oven	30	5 hours
	40	5 hours
	50	5 hours
	60	5 hours
	70	5 hours
	80	5 hours
Freezer	12	12 days
	6	12 days
	0	12 days

The lemons fruits were cut into round slices of approximately 1 cm thick and arranged at different temperature conditions and time intervals in closed glass vessels. After a predetermined time interval the slices were squeezed to discharge their juice into a pre-washed beaker and the seeds were carefully picked out from the juice. From the juice, the vitamin C content was determined by titration. A 15 mL aliquot of each juice was titrated against a standard 5.6076×10^{-3} M iodine solution to a light blue end point using freshly prepared starch as indicator [3]. The experimental data are presented in Tables 2 and 3.
The experimental data were plotted in *Temperature – Vitamin C content, Time – Vitamin C content* coordinates and linear regression techniques, involving the method of least squares were used to reveal the best-fit equation. Microsoft Excel™ 2007 spreadsheets and CurveExpert® software were used to establish the equations.

Table 2. *Variation in time of vitamin C concentration in dry oven conditions*

Temperature	**Dry oven 30 °C**		**Dry oven 40 °C**	
	Time interval [hours]	**Amount [mg/100 g]**	**Time interval [hours]**	**Amount [mg/100 g]**
	1	47.23	1	44.99
	2	46.49	2	43.34
	3	45.15	3	39.22
	4	43.67	4	36.94
	5	42.00	5	35.07
	Initial amount 47.90 mg/100 g		Initial amount 45.72 mg/100 g	
Temperature	**Dry oven 50 °C**		**Dry oven 60 °C**	
	Time interval [hours]	**Amount [mg/100 g]**	**Time interval [hours]**	**Amount [mg/100 g]**
	1	42.49	1	40.87
	2	41.18	2	37.44
	3	37.84	3	35.16
	4	34.37	4	31.58
	5	32.45	5	29.07
	Initial amount 44.10 mg/100 g		Initial amount 41.83 mg/100 g	
Temperature	**Dry oven 70 °C**		**Dry oven 80 °C**	
	Time interval [hours]	**Amount [mg/100 g]**	**Time interval [hours]**	**Amount [mg/100 g]**
	1	39.26	1	34.26
	2	34.58	2	30.62
	3	30.54	3	27.15
	4	26.58	4	19.14
	5	22.46	5	07.40
	Initial amount 41.11 mg/100 g		Initial amount 39.81 mg/100 g	

Table 3. *Variation in time of vitamin C concentration in freezer conditions*

Time interval [days]	**Freezer 12 °C**	**Freezer 6 °C**	**Freezer 0 °C**
	Amount [mg/100 g]	**Amount [mg/100 g]**	**Amount [mg/100 g]**
2	45.03	46.31	46.89
4	43.78	44.50	46.32
6	39.41	43.97	44.97
8	35.90	40.41	43.09
10	34.09	39.20	42.00
12	33.34	37.67	40.80
	Initial amount 46.34 mg/100 g	Initial amount 47.12 mg/100 g	Initial amount 47.15 mg/100 g

RESULTS AND DISCUSSIONS

The vitamin C losses determined in experimental conditions are presented in Table 4.

Table 4. *The decrease in vitamin C concentration at various temperature conditions*

No.	Temperature [°C]	Initial concentration [mg/100 g]	Final concentration [mg/100 g]	Losses [mg/100 g]	Losses [%]
For 12 days interval – freezer					
1	0	46.89	40.80	06.09	12.98
2	6	46.31	37.67	08.64	18.65
3	12	45.03	33.34	11.66	25.89
For 5 hours interval – dry oven					
4	30	47.23	42.00	05.23	11.03
5	40	44.99	35.07	09.92	20.51
6	50	42.49	32.45	10.04	23.62
7	60	40.87	29.07	11.80	28.80
8	70	39.26	22.46	16.80	42.79
9	80	34.26	07.40	26.86	78.42

The graphic representations of vitamin C content variation in time at dry oven temperatures are presented in Figure 1.

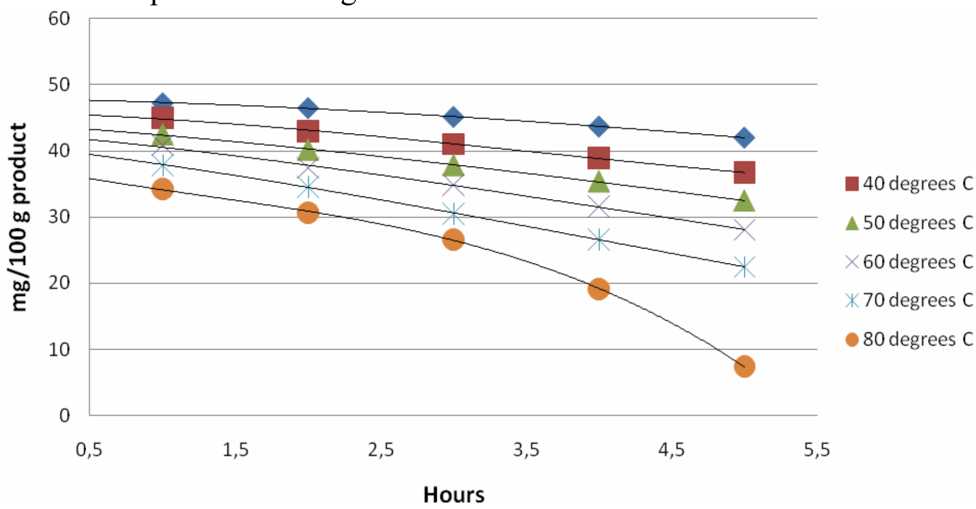

Figure 1. *Variation of vitamin C concentration for 5 hours in dry oven*

The graphic representations of vitamin C content variation in time and at freezer temperatures are presented in figure 2.
Since the experimental conditions were changed, regarding the variation of the exposure time from hours in dry oven conditions at days for freezer conditions, two different mathematical models were created for the vitamin C content evolution.
Using Microsoft Excel™ 2007 spreadsheets and CurveExpert® software, a 3rd degree polynomial correlation between time and vitamin C content, at experimental temperatures has been established for dry oven conditions:

$$\text{Vitamin C content} = A\cdot\tau^3 + B\cdot\tau^2 + C\cdot\tau + D \qquad (1)$$

For consistency in mathematical analysis were use the characteristic equations (trendline) for each determination at experimental conditions. The differences from the start point for each curve (determinate by different initial composition in vitamin C of lemon slices) were removed (Figure 3).

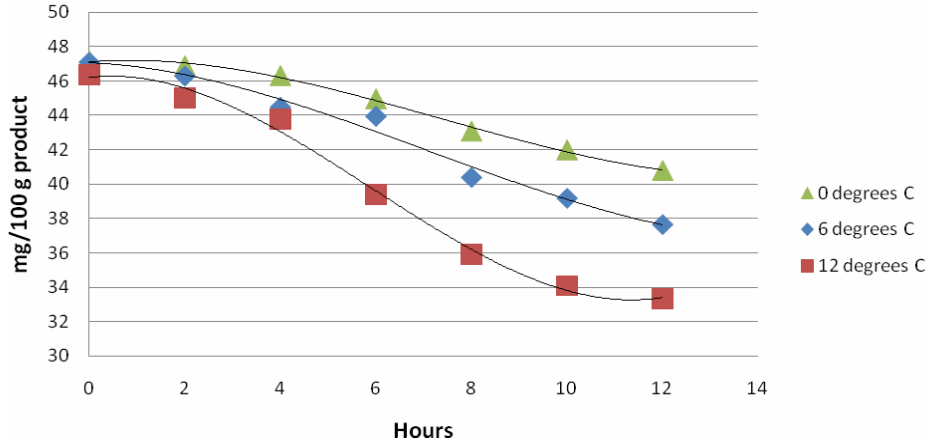

Figure 2. *Variation of vitamin C concentration for 12 days in freezer*

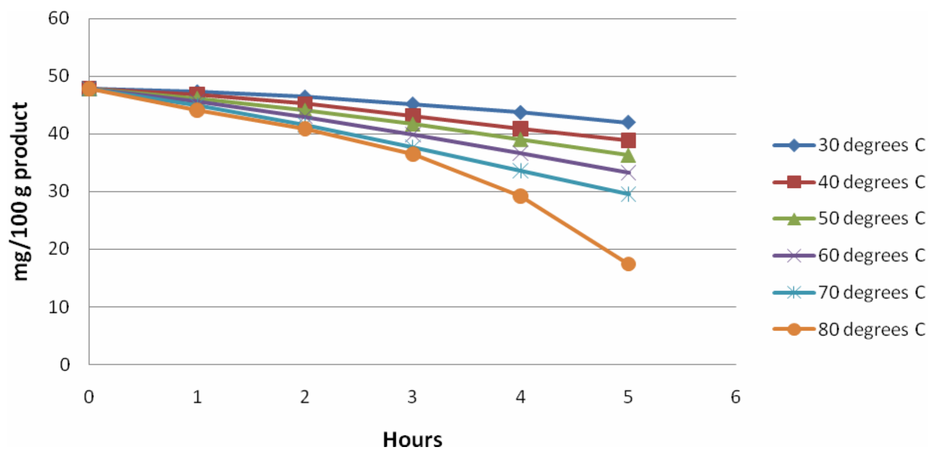

Figure 3. *Variation of vitamin C concentration for 5 hours in dry oven – modified equations*

The *A, B, C* and *D* values are presented in Table 5. The regression coefficients are greater than 0.98, thus indicating a good correlation of variables.

Table 5. *Coefficients for equation (1)*

Temperature [^{0}C]	*A*	*B*	*C*	*D*	R^2
30	0.0072	-0.1963	-0.3766	47.877	0.9989
40	0.0443	-0.4716	-0.5617	47.877	0.9815
50	0.0134	-0.238	-1.4566	47.877	0.9826
60	0.0236	-0.3226	-1.8988	47.877	0.9962
70	0.0307	-0.3827	-2.5233	47.877	0.9996
80	-0.2808	1.0986	-4.5627	47.877	0.9957

In order to correlate *A*, *B,* and *C* coefficients with temperature more models were used in CurveExpert® software (1st, 2nd and 3rd degree polynomial equations, "vapor pressure" model, "heat capacity" model, etc.). The best fit for mathematical model final form is the linear equation (Table 6):

$$Coefficient = a \cdot T + b \qquad (2)$$

Table 6. *Coefficients for equation (2)*

Coefficient	*a*	*b*
A	0.0003	0.0107
B	-0.0022	-0.2103
C	-0.0563	1.4519

The proposed model final form (empiric equation) in this paper in order to correlate variation of vitamin C content with temperature (between 303 and 353 K) and time (between 0 and 5 hours), excepting the values for 80 °C at 4 and 5 hours interval is:

$$\text{Vitamin C content} = (0.0003 \cdot T + 0.0107) \cdot \tau^3 + (-0.0022 \cdot T - 0.2103) \cdot \tau^2 + \\ + (-0.0563 \cdot T + 1.4519) \cdot \tau + 47.877 \qquad (3)$$

For a better determination of vitamin C composition at 80 °C in a time range between 0 and 5 hours, and mostly after 4 hour interval, the mathematical model is:

$$\text{Vitamin C content} = -0.2808 \cdot \tau^3 + 1.0986 \cdot \tau^2 - 4.5627 \cdot \tau + 47.877 \qquad (4)$$

For freezer conditions, using Microsoft Excel™ 2007 spreadsheets and CurveExpert® software, a 3rd degree polynomial correlation between time and vitamin C content, at experimental temperatures has been established:

$$\text{Vitamin C content} = U \cdot \tau^3 + M \cdot \tau^2 + N \cdot \tau + Z \qquad (5)$$

The *U, M, N* and *Z* values are presented in Table 7. The regression coefficients are greater than 0.98, thus indicating a good correlation of variables.

Table 7. *Coefficients for equation (5)*

Temperature [^{0}C]	*U*	*M*	*N*	*Z*	R^2
0	0.0061	-0.1355	0.2177	47.102	0.9968
6	0.0061	-0.1292	-0.1092	47.051	0.9824
12	0.0202	-0.3586	0.3274	46.198	0.9940

In order to correlate *U, M, N* and *Z* coefficients with temperature, more models were used in CurveExpert® software (1st. 2nd and 3rd degree polynomial equations, "vapor pressure" mode, "heat capacity" model etc.). The best mathematical model final form is represented by a linear equation (Table 8).

$$Coefficient = m \cdot T + n \qquad (6)$$

The proposed model final form (empirical equation) in this paper in order to correlate variation of vitamin C content with temperature (between 273 and 285 K) and time (between 0 and 12 days) is:

$$\text{Vitamin C content} = (0.0012 \cdot T + 0.0038) \cdot \tau^3 + (-0.00186 \cdot T - 0.0962) \cdot \tau^2 + \\ + (-0.0091 \cdot T + 0.0905) \cdot \tau + (-0.0753 \cdot T + 47.236) \quad (7)$$

Table 8. *Coefficients for equation (6)*

Coefficient	*m*	*n*
U	0.0012	0.0038
M	-0.00186	-0.0962
N	0.0091	0.0905
Z	-0.0753	47.236

Considering the thermal destruction of vitamin C a reaction of first-order kinetics:

$$C_A = C_{A_0} \cdot e^{-k \cdot t} \quad (8)$$

Arrhenius noted that the $k(T)$ data for many reactions fits the equation:

$$k = k_0 \cdot e^{-\frac{E_a}{R \cdot T}} \quad (9)$$

where k_0 and E_a are constants characteristic of the reaction and R is the gas constant. E_a is the activation energy and k_0 is the pre-exponential factor, or the Arrhenius factor. The measurement units of k_0 are the same of those of k. E_a is usually expressed in kcal/mol or kJ/mol.
Taking logs of equation (9), it gets:

$$\log k = \log k_0 - \frac{E_a}{2.303 \cdot R} \cdot \frac{1}{T} \quad (10)$$

If the Arrhenius equation is obeyed, a plot of log k versus $1/T$ is a straight line with the slope $-E_a/(2.303 \cdot R)$ and the intercept log k_0. This allows finding E_a and k_0.
Using equation (8) and corrected values from experimental data, log k is calculated at the values presented in Tables 9 and 10. The data separation is necessary because of experimental time interval even that the results are reported at seconds.

Table 9. *Log k values for dry oven conditions*

Time [hours]	Temperature [°C]					
	30	40	50	60	70	80
1	-5.48	-5.24	-5.00	-4.88	-4.76	-4.67
2	-5.36	-5.10	-4.94	-4.82	-4.71	-4.65
3	-5.27	-5.02	-4.90	-4.77	-4.65	-4.61
4	-5.20	-4.96	-4.85	-4.73	-4.61	-4.56
5	-5.14	-4.93	-4.81	-4.69	-4.57	-4.49

In activation energy calculus is necessary to take in consideration that the lemons were sliced and there is a particular heat and mass transfer mechanism inside slices. In the first stage, due to the heat action at lemons' surface, the vitamin C near the surface was first reduced. In the second stage, a certain time is required for vitamin C to migrate, due to the gradient concentration from inside to surface and for temperature to level inside slices. When the temperature inside slices is homogeneous the destruction of vitamin C is different according to the temperature intensity.

Table 10. *Log k values for freezer conditions*

Time [days]	Temperature [°C]		
	0	6	12
2	-6.78	-7.00	-7.49
4	-7.09	-7.08	-7.59
6	-6.51	-6.87	-7.04
8	-6.43	-6.65	-6.89
10	-6.45	-6.67	-6.87
12	-6.50	-6.67	-6.86

These phenomena are responsible for the changes of the equations slopes in the graphic representations of log *k* values versus 1/*T* (Figures 4 and 5).

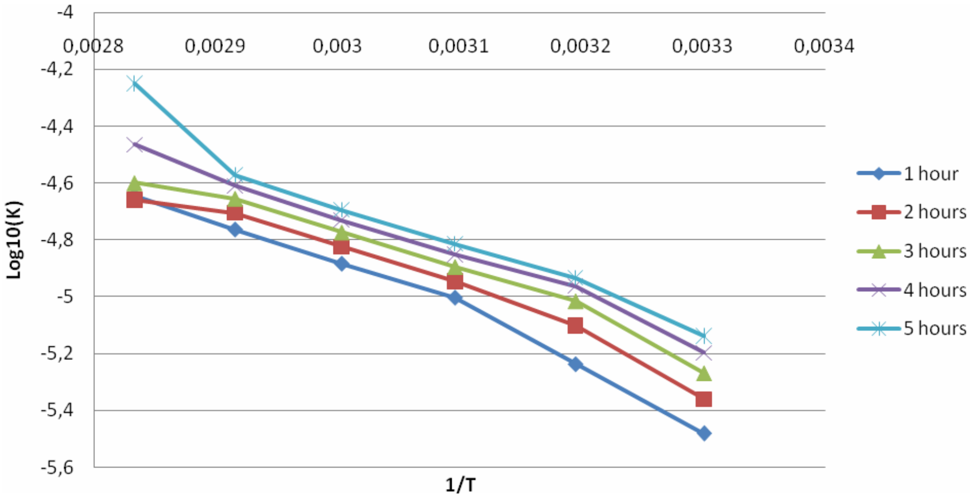

Figure 4. *Variation of log k in temperature interval and 5 hours, in dry oven*

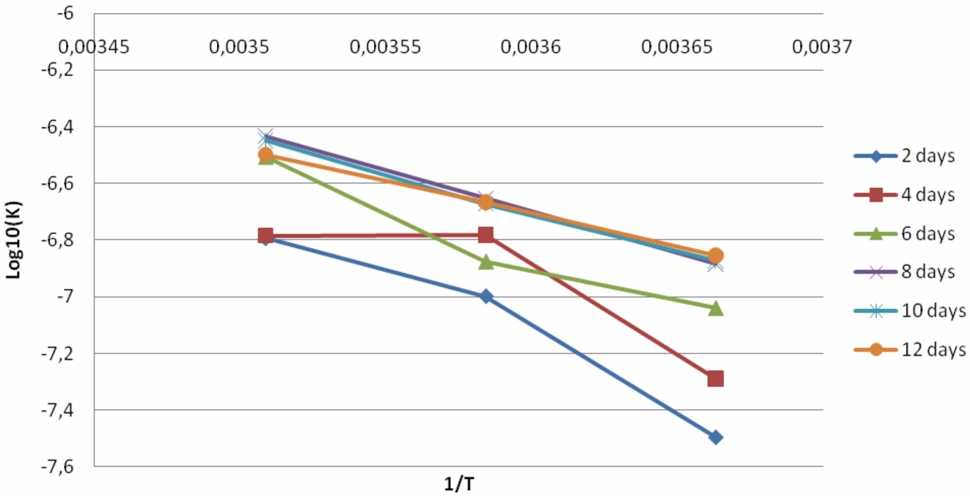

Figure 5. *Variation of log k in temperature interval and 12 days, in freezer*

The values of activation energy are presented in Tables 11 and 12.

Table 11. *The equations and activation energy for experimental data in dry oven*

Time [hours]	Equation	Temperatures range [°C]	E_a	
			[cal/mol]	[kJ/mol]
1	y = -2339.8x + 2.2401	30 – 50	10707.07	44.863
	y = -1403.5x - 0.6705	50 – 80	6422.50	26.910
2	y = -2457.9x + 2.7516	30 – 40	11247.50	47.127
	y = -1325.8x - 0.8412	40 – 80	6066.94	25.420
3	y = -2402.5x + 2.6598	30 – 40	10993.99	46.065
	y = -1331.9x - 0.7723	40 – 80	6094.85	25.537
4	y = -2224.2x + 2.1437	30 – 40	10178.07	42.646
	y = -1338.9x - 0.7077	40 – 80	5781.39	24.224
5	y = -1930.8x + 1.2353	30 – 40	8835.45	37.021
	y = -1294.6x - 0.8016	40 – 70	5924.16	24.822
	y = -3879.5x + 6.7394	80	17752.82	74.384

As can be seen from data in Table 11, at low temperatures (30, 40 °C), regardless the time, the activation energy is around 45 kJ/mol (≈ 10.78 kcal/mol). This value denotes a chemical reaction, most probably the decomposing reaction of ascorbic acid to diketo-gulonic acid [4]. At higher temperatures (40 – 80 °C), the activation energy is only 25 kJ/mol (≈ 6 kcal/mol), denoting rather a transport process (of mass and/or heat) than a chemical reaction. We may say that at lower temperatures the process is reaction-driven whereas at higher temperatures, when chemical reactions are accelerated (according to Arrhenius equation) the process is limited by transport and transfer phenomena.
Supporting this conclusion are the data from Table 12, showing that at low temperatures (0 – 12 °C) the activation energy varies between 52.6 and 87.4 kJ/mol, denoting a chemical reaction-driven process.

Table 12. *The equations and activation energy for experimental data in freezer*

Time [days]	Equation	Temperatures range [°C]	E_a	
			[cal/mol]	[kJ/mol]
2	y = -4559.1x + 9.2502	0 – 12	20862.71	87.415
4	y = -3941.9x + 7.215	0 – 12	18038.37	75.581
6	y = -3454x + 5.5773	0 – 12	15805.71	66.226
8, 10, 12	y = -2747.3x + 3.1854	0 – 12	12571.81	52.676

CONCLUSIONS

According with theoretical and experimental researches it is clear that the amounts of vitamin C in lemon are influenced by the nature, intensity and time exposure at heat treatments or usual/recommended storage temperature.
When increasing temperature, the quantity of vitamin C drops significantly: after 5 hours of thermal processing, vitamin C losses increase from 11.03% at 30 °C to 78.42% at 80 °C. For freezer conditions, in a 12 days period, vitamin C losses increase from 12.98% at 0 °C to 25.89% at 12 °C.

At low temperatures (up to 35 – 40 °C) the decay process of vitamin C in lemon slices is governed by the chemical reaction of ascorbic acid decomposition, meanwhile at more elevated temperatures (40 – 80 °C) the transport and transfer phenomena are giving the global process rate.

The proposed mathematical models permit a simulation of the vitamin C degradation rate in lemon slices in case of exposure to thermal treatments and also to determine the possible final concentration in vitamin C knowing the initial amount and the duration of thermal processing.

Knowing the activation energy values for presented experimental conditions and initial concentrations of vitamin C, using the equations (8) and (9), and only for these thermal conditions, we can determine the final concentration in vitamin C, or the rate of destruction of vitamin C in lemon slices.

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