Mathematical Modelling of Some Nutrient Losses During Heat Treatment of Stewed Apples

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Abstract: Vitamin C (later noted VITC) and polyphenols (later noted PP) were regarded as main nutritional markers in the transformation process of stewed apples after an *in situ* measurement campaign at two leading French industrials on that matter. Experiments on pilots with the CTCPA of Avignon made it possible to create a small experimental data base whose treatment is the core of this article. The objective of this work is to check if the experimental data collected at the CTCPA facility can be represented by a single model of 2 separate first order reactions, with or without Arrhenius, under varying processing temperatures.

Keywords: vitamin C; polyphenols; model; reaction; Arrhenius

INTRODUCTION

Vitamin C (later noted VITC) and polyphenols (later noted PP) were regarded as main nutritional markers in the transformation process of stewed apples after an *in situ* measurement campaign at two leading French industrials. Experiments on pilots with the CTCPA of Avignon made it possible to create a small experimental data base whose treatment is the core of this article. A short bibliographical study on ScienceDirect.com showed that there was no article available on the modelling of the degradation of the vitamin C in stewed apples. There are on the other hand some articles treating this subject in other products (fruits, potatoes). The modelling of the kinetics is usually done with a first order reaction with temperature dependence (Arrhenius). Concerning polyphenols, there is not any article on ScienceDirect.com that studies its kinetics of thermal degradation. The only reference found close to this subject was a paper that models the thermal decomposition of the polyphenol oxydase by a first order reaction. The objective of this work is to check if the experimental data collected at the CTCPA facility can be represented by a single model of first order reaction with or without Arrhenius (separately for vitamin C and polyphenols).

MATERIAL AND METHODS

A mix of Golden, Granny and Gala apple varieties (v/v/v ; 2/1/1) were received directly from the industry. The two different processes employed in industry are detailed in Figure 1. Their main difference is situated in the first heat treatment. Indeed, the process named hot break, implies the heat treatment step after the refining step and it is the contrary in the cold break process. In this case, the heat treatment of the hot break process is higher than in the clod break.

To model the behaviour of the nutritional markers during the transformation process, seven and five trials respectively for the hot and the cold break (repeated 3 times) were led by modifying the following parameters.

Experimental plan. The boxes with a star mean that this step (and the following) was not realised.

Step	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6	Trial 7
Washing	Room temperature, 5 min						
Crushing	Ascorbic acid added 65 g/l						105 g/l
Heat-treatment	80°C/15 min			80°/5	90°/5	90°/15	*
Refining	1.25 mm		0.5	*	*	*	*
Concentration pasteurisation	83°C/1	90°C/1	*	*	*	*	*
Packaging		*	*	*	*	*	*
Cooling	6°C/50°C	*	*	*	*	*	*

Sample preparation. Four samples (200 g each) were taken each step and immediately packaged in a small boat, frozen and stored at 20°C until analysis.

Material and solvents standards. All solvents were of the highest analytical grade. Reference compounds, reagents and solvents from Sigma-Aldrich Chimie (Saint Quentin Fallavier, France).

Vitamin C analysis. Vitamin C was quantified by HPLC (Waters system) using an isocratic gradient equipped with a reverse phase column C_{18} (Waters, Spherisorb ODS 2) (5 µm packing) (250 × 4.6 mm id). Ascorbic acid was eluted under the following conditions: injected volume 20 µl; oven temperature 30°C; solvent mixture [K_2HPO_4, 0.1M; KH_2PO_4, 0.08M; MeOH, 55/25/20, v/v/v). Flow rate was 1.5 ml/min and total elution time was 10 min. Detection was performed by a III-1311 Milton Roy fluorimeter (Ivyland, U.S.) with $\lambda_{excitation}$ = 350 nm and $\lambda_{emission}$ = 430 nm. Quantification was carried out by external calibration with ascorbic acid. Calibration curve was set from 1 to 7 µg/ml of ascorbic acid.

Determination of polyphenol content. Frozen material (from 300 mg to 1 g) was homogenised with 10 ml of extraction solution (acetone/water, 7/3, v/v) for 10 min. The raw extract was obtained after filtration (Whatman®, England). The complete analytical procedure was performed as per Georgé *et al.* (2005). Polyphenols are commonly determined using Folin-Ciocalteu reagent that interacts with other different reducing non-phenolic substances and leads to an overestimation of polyphenol content. In our method, solid phase extraction (Oasis HLB) was carried out on the raw extract in order to eliminate the water-soluble reducing interferences including vitamin C. Colorimetric correction was thus performed by subtracting interfering substances contained in the water washing extract to the raw extract.

Modelling and identification. The degradation kinetics of the vitamin C is usually modelled by a first order reaction whose equation is:

$$\frac{dC}{dt} = -k \times C \qquad (1)$$

where: C – concentration in mg/100g of dry matter
k – temperature dependence of Arrhenius type:

$$k = k_0 e^{\frac{-E_a}{RT}}$$

where: T – product temperature expressed in Kelvin
E_a – energy of activation and R the constant of the perfect gases

All calculations are carried out with SCILAB and its *lsqrsolve* routine (Levenberg Marquardt algorithm). The criterion used here is the sum of the squares balanced by the experimental standard deviations. The case of polyphenols is treated in an equivalent way.

RESULTS AND DISCUSSION

Vitamin C

Initially, only the data of hot break were used to identify the unknown parameters 0 and *a*. This global adjustment gives k_0 = 8.814e9 and E_a = 88 907 J/mole. The same set of parameters is then used to simu-

Table 1. Some comparable parameters found in the bibliography (Cameron *et al.* 1955 cited by Villota & Hawkes 1992)

Product	k_0	E_a
Processed apricot	1.770e+09	99 208
Processed grapefruit	1.640e+07	86 650
Processed orange juice	6.264e+09	10 172
Processed tomatoes	27.6	55 674

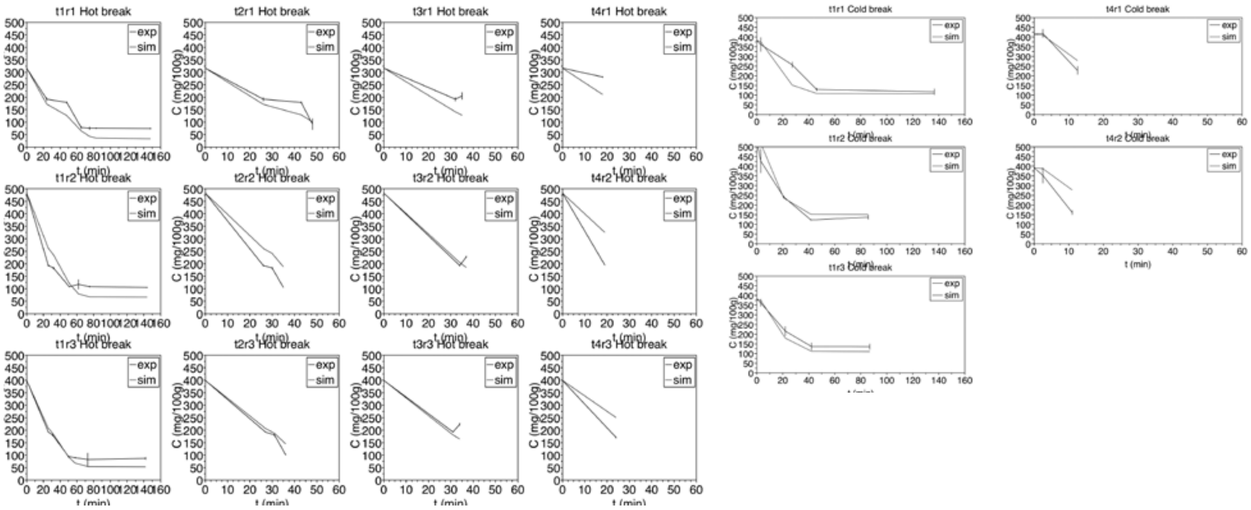

Figure 1. Validation of the set of optimal parameters for the vitamin C on all hot break (left) and cold break (right) trials. The curves in black with error bars are the experimental values and the curves in blue are simulated. Observed average error: 30 mg/100 g i.e. 21% in relative value for hot breaks and 14.4% for cold breaks. "t1r1" means "trial 1 repetition 1"

late the entire experimental conditions available [Figure 1 in the (6°C, 90°C) range]. The average relative error is 14.5% for cold break and 21% for hot break. In absolute value, that makes an average error of 30 mg/100 g. Insofar as the average standard deviation on the measures (which is an underestimate of experimental uncertainties) is of 12–13 mg/100 g, it can be noted that the average modelling error is comparable with the size of 3 standard deviations what remains reasonable.

In Cameron *et al.* (1955) quoted by Villota and Hawkes (1992), very similar data for other processed fruits are available (see Table 1). It is for the energy of activation that the greatest similarities are found.

Polyphenols

In the same way, only data relative to hot break experiments were considered because those of cold

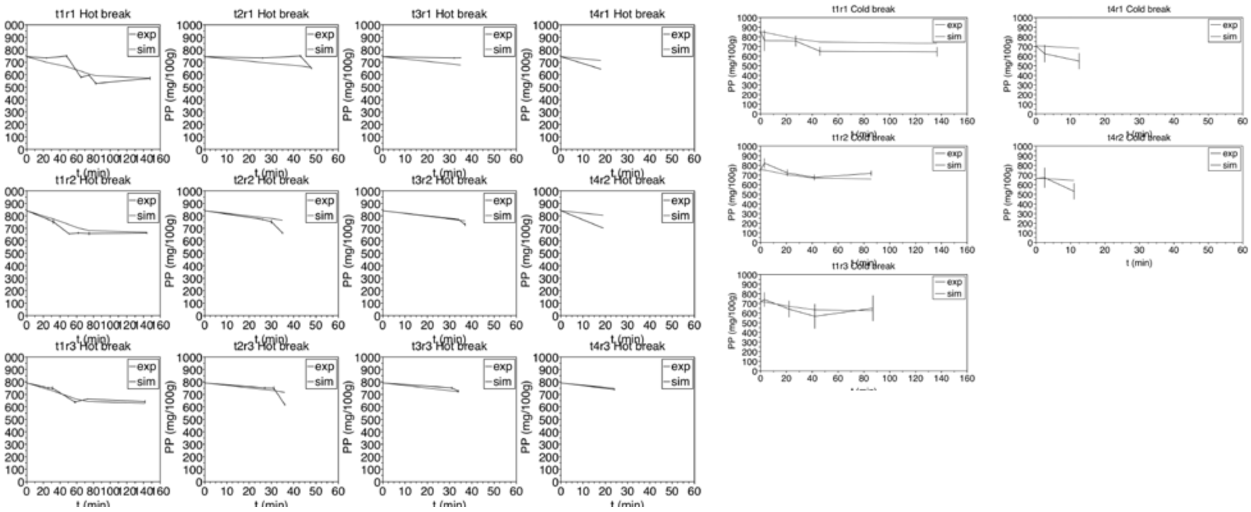

Figure 2. Validation of the set of optimal parameters for the polyphenols on all hot (left) and cold (right) break trials. The curves in black with error bars are the experimental values and the curves in blue are simulated. Observed average error: 42 and 39 mg/100 g, i.e. 6.5 and 5.9% in relative value for cold and hot breaks, respectively. "t1r1" means "trial 1 repetition 1"

break are well too of doubtful validity. The identification procedure on cold break kinetics gives an optimum at k_0 = 14.19 and E_a = 36 420 J/mole. Validation on the all kinetics of both cold break and hot break gives an average error of 40 mg/100 g or approximately 6% what is rather very good (Figure 2).

References

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